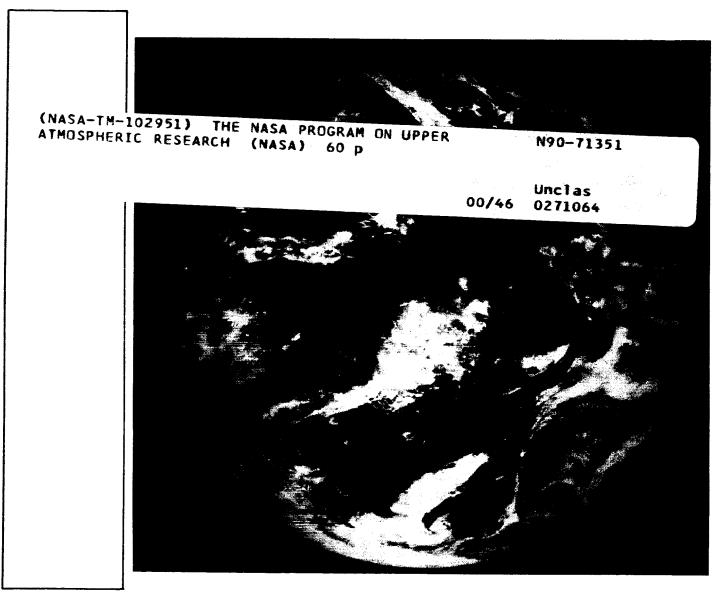
# PROGRAM PLAN

# The NASA Program on Upper Atmospheric Research

June 1976





UPPER ATMOSPHERIC RESEARCH OFFICE OFFICE OF SPACE SCIENCE WASHINGTON, D. C. 20546

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# **GLOSSARY**

ABRL Army Ballistic Research Laboratories

AE Atmospheric Explorer
AEC Atomic Energy Commission

AFGL Air Force Geophysics Laboratory

AIBS American Institute of Biological Sciences

AMPS Atmosphere, Magnetosphere and Plasmas-in-Space
ARAP Aeronautical Research Associates of Princeton

ARC Ames Research Center

ARPA Advanced Research Projects Administration
BUVS Backscattered Ultraviolet Spectrometer
CEO Council on Environmental Quality

CFM Chlorofluoromethanes

CIAP Climatic Impact Assessment Program

CIC Climatic Impact Committee

COMESA Committee on Meteorological Effects of Stratospheric Aircraft

COSPAR Committee on Space Research

COVOS Comité d'Études des Consequences des Vols Stratosphériques

CNES Centre Nationale d'Études Spatiales
CPSC Consumer Products Safety Commission

DOA Department of Agriculture
DOC Department of Commerce
DOD Department of Defense
DOI Department of the Interior
DOS Department of State

DOT Department of Transportation
EEPO Environmental Effects Project Office
EPA Environmental Protection Agency
ERB Earth Radiation (Energy) Budget

ERDA Energy Research and Development Administration

ESA European Space Agency

EUVS Extreme Ultraviolet Spectrometer FAA Federal Aviation Administration

FCST Federal Council for Science and Technology
GARP Global Atmospheric Research Program

GASP Global Air Sampling Program
GCM General Circulation Model

GFDL Geophysical Fluid Dynamics Laboratory
GISS Goddard Institute for Space Studies
GMCC Global Monitoring for Climatic Change

GSFC Goddard Space Flight Center
HAPP High-Altitude Pollution Program
HSI High-Speed Interferometer

IAC Institute for Advanced Computation

IAGA International Association of Geomagnetism and Aeronomy

IAMAP International Association for Meteorology and Atmospheric Physics

ICAS Interdepartmental Committee for Atmospheric Sciences

IITRI Illinois Institute of Technology Research Institute

ILLIAC Illinois Advanced Computer

IMOS Inadvertent Modification of the Stratosphere

JPL Jet Propulsion Laboratory
JSC Johnson Space Center
LaRC Langley Research Center
LeRC Lewis Research Center
LIDAR Light Detection and Ranging

LIMS Limb Scanning Infrared Measurements of the Stratosphere

MAP Middle Atmosphere Program

MCA Manufacturing Chemists Association
MIT Massachusetts Institute of Technology
MOU Memorandum of Understanding
NAS National Academy of Sciences

NASA National Aeronautics and Space Administration

NAE National Academy of Engineering
NBS National Bureau of Standards

NCAR National Center for Atmospheric Research

NCAR/UC NCAR/University of Colorado

NOAA National Oceanic and Atmospheric Administration

NSSDC National Space Science Data Center NSF National Science Foundation

OA Office of Applications

OAST Office of Aeronautics and Space Technology

OSF Office of Space Flight
OSS Office of Space Science
POP Program Operating Plan
ppbv Parts per billion by volume

RTOP Research and Technology Operating Plan
SAGE Stratospheric Aerosol and Gas Experiment
SAM II Stratospheric Aerosol Measurement

SAMS Stratospheric and Mesospheric Sounder
SBUV/TOMS Solar and Backscattered Ultraviolet Spectrometer/Total Ozone Mapping

System

SCOSTEP Special Committee on Solar Terrestrial Physics

SIMS Subcommittee on Instrumentation and Measuring Systems

SRB Solid Rocket Booster SRM Solid Rocket Motor

SR&T Supporting Research and Technology

SST Supersonic Transport

UARO Upper Atmospheric Reseach Office
UCI University of California, Irvine
UCLA University of California, Los Angeles
URSI International Union of Radio Science

USU Utah State University WFC Wallops Flight Center

WMO World Meteorological Organization

#### **FOREWORD**

The NASA Program on Upper Atmospheric Research presents NASA's plans for reducing many of the existing uncertainties in our understanding of the physics and chemistry of the Earth's upper atmosphere through the acquisition and analysis of scientific knowledge. The plan focuses on the application of this knowledge to problems of national concern, especially those related to the stratosphere. These include the evaluation of the possible effects of the continued atmospheric release of chlorofluoromethanes, operation of the Space Shuttle Transportation System and increased aircraft operations in the lower stratosphere.

The plan, generated in response to the assignment given to NASA by the US Congress through the FY 1976 NASA Authorization Act, outlines a comprehensive program of research, technology, and monitoring of stratospheric phenomena and indicates the means by which this program will be implemented by NASA centers, universities, and industry. It addresses cooperation with other federal agencies, professional organizations, and the international community. The responsibility for developing and implementing the NASA Plan has been given to the Director of the Upper Atmospheric Research Office. The Director is also responsible for modifying the plan as program results require or as new national concerns arise. We anticipate that program results will be reported by individual investigators in the scientific literature. However, to hasten the exchange of scientific results, NASA will assist in sponsoring workshops, national and international conferences, and newsletters.

Although this plan is primarily a discussion of the activities within and supported by NASA, brief references are made to the related programs of other Federal agencies and to relations with industry and other nations. It is organized in such a manner that, if desirable and in concert with the other agencies, the plan could be amplified into a national plan for stratospheric research.

A draft of this plan was initially reviewed by the Stratospheric Research Advisory Committee, which advises NASA on its Upper Atmospheric Research Program, and by representatives from each of the NASA centers. A second draft was discussed by a group of scientists invited to a special Congressional hearing (Feb. 15, 1976) on the plan. The second draft was also reviewed by the members of the Interdepartmental Committee for Atmospheric Sciences (ICAS) and by the members of the Federal Task Force on Inadvertent Modification of the Stratosphere (IMOS). This current version reflects the many constructive comments received from these various sources.

Woell Hinner

Noel W. Hinners Associate Administrator for Space Science

#### I. INTRODUCTION

The purpose of the NASA Upper Atmospheric Research Program is to develop a better understanding of the physical and chemical processes that occur in the Earth's upper atmosphere with emphasis on the stratosphere, the region between 15 and 50 km. The physical and chemical processes occurring in this region are extremely complex and are only beginning to be understood, but their study has become increasingly significant in view of the possible perturbing effects caused by natural and man-made activity.

The postulate that man-made pollutants could cause harmful effects in the stratosphere was publicized in 1971 by a few scientists who had grave concerns about the effects of high-flying supersonic transports (SSTs). Their concern awakened some citizens to the possible imminent danger that pollutants in the stratosphere may reduce the ozone content, thus permitting an increase at the Earth's surface of the harmful ultraviolet portion of solar radiation. As a result, in 1971, the Climatic Impact Assessment Program (CIAP) was tormed to study the effects of ozone reduction in the stratosphere caused by subsonic and supersonic aircraft. The program was undertaken by the Federal Government, under the sponsorship of the Department of Transportation (DOT), and was formally terminated in 1975.

Shortly after the creation of CIAP, the National Academy of Sciences (NAS) established the Climatic Impact Committee (CIC) to advise DOT and, specifically, CIAP. In early 1975, CIAP released a summary of findings, and the CIC issued a report (Climatic Impact Committee, 1975) that stressed the concern regarding the possible reduction of stratospheric ozone by the NO<sub>x</sub> emissions from large fleets of subsonic and supersonic transports (SSTs).

In 1973, NASA recognized that adverse effects in the stratosphere might result from the exhaust products from the solid-rocket motors of the Space Shuttle, a reusable transportation system currently under development. Two effluents, HCl and Al<sub>2</sub>O<sub>3</sub>, could produce harmful effects by interacting with ozone and sunlight in the stratosphere. Emphasis has been placed on the study of the effects of the direct release of HCl into the stratosphere. These studies were included in the responsibilities of NASA's Program Office for Space Shuttle

Environmental Effects as part of the overall Space Shuttle program.

Meanwhile, in 1974, as a result of basic research sponsored by the Atomic Energy Commission (AEC), the first scientific paper was published (Molina and Rowland, 1974) which treated the problem of possible ozone reduction by the chlorofluoromethanes (CFMs) in widespread use as propellants in aerosol spray cans, as foaming agents, and as refrigerants. The concern was that the CFMs, very stable chemically in the lower atmosphere, would diffuse into the stratosphere and be photodissociated into active chlorine atoms and other fragments. These chlorine atoms, in turn, could react catalytically with ozone and cause the destruction of a large number of ozone molecules.

Because of the increased awareness of the problem both by the public and government, a Federal Task Force on the Inadvertent Modification of the Stratosphere (IMOS) was established by the Federal Council for Science and Technology and the Council on Environmental Quality. The task force concluded that the potential of the CFMs for causing ozone reduction was reason for concern and recommended that research efforts be accelerated.

In June 1975, the Interdepartmental Committee for Atmospheric Sciences (ICAS) Panel on Inadvertent Modification of Weather and Climate made an assessment of the ozone reduction issue (Interdepartmental Committee for Atmospheric Sciences, 1975). Its report stressed the need for chlorine measurements in the stratosphere, including direct measurements of the chlorofluoromethanes, CFC1<sub>3</sub>(F-11) and CF<sub>2</sub>C1<sub>2</sub>(F-12). Other recommendations were for a systematic search for possible chlorine sinks, an ozone monitoring program, and verification of certain reaction rates.

As part of the FY 1976 NASA Authorization Act, NASA was instructed by Congress to develop and implement a comprehensive program of research, technology, and monitoring of the phenomena of the upper atmosphere to provide for an understanding of and to maintain the chemical and physical integrity of the Earth's upper atmosphere.

The act provides that NASA arrange for participation by the scientific and engineering community, of both the nation's industrial organizations and institutions of higher education, in planning and carrying out appropriate research, in developing necessary technology, and in making necessary observations and measurements; and to make every effort to enlist the support and cooperation of cognizant scientists and engineers of other countries and international organizations.

In recognizing the need to increase and provide a better focus for NASA's efforts to understand the nature of the stratosphere, the natural forces that control it, and the effect of human activity upon it, the Associate Administrator assigned the overall responsibility for NASA's stratospheric research activities to the Office of Space Science (OSS).

In order to carry out its assignment, OSS established the Upper Atmospheric Research Office (UARO), whose purpose is to plan, direct, and implement the stratospheric research activities of NASA. For better coordination, most of the programs in research involving the stratosphere were transferred to UARO. These included stratospheric effects of Space Shuttle operations which were previously in the Office of Space Flight (OSF) and the effects of aircraft operation in the stratosphere from the Office of Aeronautics and Space Technology (OAST). The latter included the Global Air Sampling Program (GASP) in which commercial 747 aircraft are equipped with in situ sensors to measure constituents of the upper troposphere and lower stratosphere.

Approved programs related to satellite monitoring of the stratosphere remained in the original offices, e.g., the Atmospheric Explorer Program, which uses the Back-scattered Ultraviolet Spectrometer (BUVS) to measure stratospheric ozone, remained in the Solar Terrestrial Division in OSS and the responsibility for the Nimbus series of satellites, which also measures stratospheric constitutents, remained in the Office of Applications (OA); coordination among the related NASA programs occurs through a steering committee consisting of Program Managers from the different areas.

The plan described in this document focuses on the assignments and responsibilities of the UARO and includes reference to, but not an in-depth treatment of, related programs in NASA and in other Federal agencies.

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# II. GOALS AND OBJECTIVES

The overall goal of the NASA Upper Atmospheric Research Program is to acquire sufficient understanding of the physical and chemical processes occurring in the Earth's atmosphere so that:

- (1) Perturbations in the stratosphere caused by man's actions can be accurately assessed.
- (2) Any associated change in the transmission of solar radiation, particularly ultraviolet, through the stratosphere to the surface can be determined.

Within the context of this goal, long- and short-term objectives have been established. The long-term objective is to develop an organized, solid body of knowledge of the physics, chemistry, and transport processes occurring in the stratospheric region of the Earth's atmosphere. The short-term objective is to fulfill three NASA commitments:

- (1) Determine the impact of chlorofluoromethanes (CFMs), used in aerosol spray cans, as foaming agents, and as refrigerants, on stratospheric ozone, and produce a report by September 1977, which can be utilized by the appropriate regulatory agency in deciding on a course of action.
- (2) Obtain the necessary information on the effects of Space Shuttle exhaust products on stratospheric ozone in a form that can be used by the Office of Space Flight (OSF), NASA, in the preparation of a report on overall Space Shuttle environmental effects.
- (3) Acquire data on the impact of aircraft exhausts on stratospheric ozone and produce a report to be submitted to the Federal Aviation Administration.

A continuing goal of the program is to be able to understand and evaluate other potential threats to the upper atmosphere.

#### III. PROGRAM STRUCTURE

The program planning phase emphasizes the development of institutions and people to accomplish the program's goals and objectives. The focus is on the establishment of a long-term basic science program in upper atmospheric research. The long-term program gives extensive treatment to the physics and chemistry of ozone in the stratosphere including all of the factors, photochemical and dynamic, that determine the distribution of ozone and its temporal and spatial variations. Also, included as part of the long-range program are investigations of stratospheric constituents other than ozone which could affect the transmission of solar radiation through this region.

Necessary data are obtained in the basic science program through a coordinated effort involving field measurements, laboratory experiments, and theoretical studies Requirements for additional information are established in each of these areas based on our current knowledge. Also, as part of the field measurements effort, requirements are established for a global monitoring system, including the development of platforms.

Implementation of the long-range program is through financial support of institutions and people within and outside of NASA. Within the agency, the Goddard Space Flight Center (GSFC), and the Jet Propulsion Laboratory (JPL) have been asked to take major roles in implementing the goals and objectives of the long-range program. The Ames Research Center has been assigned a lead role in field measurements utilizing aircraft along with a role in theoretical studies emphasizing modeling. For the outside community, particularly the universities, the plan is to consolidate within 2 to 3 years the activities in atmospheric science through block funding instead of funding of individual proposals.

NASA plans to continue to fund outstanding proposals in upper atmospheric research and encourage universities to strengthen their atmospheric science capabilities so that they can evolve as a center of excellence in atmospheric science. A "Dear Colleague" letter encouraging the scientific community to submit unsolicited proposals for consideration in this program is planned for release in the summer of 1976.

While the long-term program is being established, it has become necessary to consider how man's actions are presently affecting the stratosphere. Some of the actions that have been identified for assessment include: (1)

Space Shuttle operations in the stratosphere, (2) aircraft flight in the upper troposphere and lower stratosphere and (3) the release of chlorofluoromethanes (CFMs), used in aerosol spray cans, as foaming agents and as refrigerants. These potential threats to the stratosphere are included in a short-term assessment program that can be viewed as a subset of the longer term basic science program. The steps in the assessment are to: (a) gather the pertinent data including new measurements, (b) use these data in existing mathematical models to predict future effects, (c) evaluate and compare results with the original hypothesis, and (d) recommend corrective action, if warranted. Each of the assessments results in a report to be issued to appropriate authorities for use in the decision-making processes.

#### LONG-TERM BASIC SCIENCE PROGRAM

The Basic Science program is designed to understand all of the factors, photochemical, chemical and dynamic, that determine the distribution of ozone and its temporal and spatial variations in the upper atmosphere. The Basic Science program is also designed to understand factors, other than ozone, that affect the transmission of solar radiation through the stratosphere.

# **Stratospheric Chemistry**

Ozone, the most important of the trace constituents in the stratosphere, forms a protective layer which absorbs harmful solar ultraviolet light and greatly reduces its intensity at the Earth's surface. Ozone in the stratosphere is believed to be responsible for the increase of temperature with height, the phenomenon that distinguishes that region from the troposphere and the mesophere. Because of ozone's unique properties, changes in stratospheric ozone concentrations can affect the UV flux at the Earth's surface and the temperature in the lower stratosphere with corresponding changes in the Earth's weather and climate

Factors that influence ozone concentrations in the stratosphere are the photochemistry initiated by solar radiation, large scale dynamics of the stratosphere, and the chemical transitions produced by chemically active species.

Chapman (1930) was the first to formulate the mechanism of ozone photochemistry in the upper atmosphere. His mechanism involves the photodissociation of molecular oxygen, O<sub>2</sub>, by solar UV radiation of wavelength less than 242 nm:

$$O_2 + h\nu \rightarrow 2O$$

Formation of atomic oxygen, O, peaks in the altitude region of 80 to 120 km, although the reaction proceeds at a significant rate down to an altitude as low as 30 km. Because of this reaction, oxygen atoms are one of the major atmospheric species at altitudes above 80 km. Below 80 km the oxygen atoms react with molecular oxygen to form ozone by the three-body recombination:

$$O + O_2 + M \rightarrow O_3 + M$$

where M is any third body, mainly  $N_2$  or  $O_2$ . The ozone in turn, can be photodissociated by solar radiation and can also enter into a destruction reaction with atomic oxygen:

$$O_3 + h\nu \rightarrow O_2 + O$$

and

$$0_3 + 0 \rightarrow 20_2$$

These sets of reactions which transform solar radiation energy into thermal energy are responsible for the major features of the temperature profile in the stratosphere.

Requirement: Measure the O concentration and monitor the solar radiation in the mesosphere and upper stratosphere to better understand the formation of ozone.

Although ozone is formed in the regions above 30 km, its maximum concentration is found near 17 km over the winter hemisphere pole, near 25 km over the equator, and near 22 km over the summer hemisphere. Ozone densities (total column content) show both longterm and short-term variations. The natural long-term trends (some possibly connected to the 11-year solar cycle) are on the order of 5 percent in a decade. At mid-latitudes, the daily variations average almost 10 percent in winter and 5 percent in summer. There is an approximately 25 percent annual variation and a 2 percent quasi-biennial variation. It is believed that large day-to-day changes are due to the transport by winds of ozone-rich or poor air from one area to another. The large seasonal variations are thought to represent a natural cyclic behavior that is part of the normal climate and climate variability.

Requirements: Globally monitor ozone to study its variability.

Investigate the large-scale dynamics of the stratosphere in order to better understand stratospheric climate and climate variability.

Many trace constituents are postulated to influence the ozone chemistry and physics in the upper atmosphere. In this category are the oxides of hydrogen ( $HO_x$ ), nitrogen ( $NO_x$ ), chlorine ( $CIO_x$ ) and possibly other halogenated compounds. Anderson (1976) has developed a scheme to investigate the reactions of these compounds with ozone. The scheme consists of three parts:

- (1) Chemical source terms, which represent the upward flow of stable polyatomic molecules from the Earth's surface and troposphere.
- (2) Linking *radicals* or molecular fragments which are formed directly (and irreversibly) from the chemical source terms either by photolysis or by chemical reaction and are the primary reactants with ozone.
- (3) Reservoir or sink terms which are formed by the recombination of the radicals, recycled into the radical system by photolysis and chemical reactions and removed by downward and meridional transport.

The relations between the parts are shown in Fig. 1. The source and sink terms are relatively stable chemically, having chemical lifetimes on the order of weeks to months so that their global distribution is, in general, governed by transport processes rather than by details of the local chemical environment. The degree to which this is true provides an important spectrum of tracers for horizontal and vertical transport processes. In contrast, the radicals have chemical lifetimes on the order of minutes and they thus reflect, with considerable alacrity, the chemical conditions in their immediate vicinity. Details of the various sytems are given in the following paragraphs.

#### The Hydrogen System

The relationships between the three parts in the hydrogen system are shown in Fig. 2. Methane, produced principally by bacteria in marsh lands and lakes, (Ehhalt, 1972) diffuses upward and reacts with  $O(^1D)$  in the stratosphere to produce OH. The methyl radical is eventually converted to  $CO_2$  after further release of hydrogen to the  $HO_X$  system, which consists principally of OH, H and  $HO_2$ . These three hydrogen radicals are interconverted very rapidly by reaction with ozone and

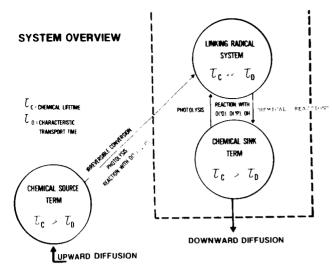


Figure 1

atomic oxygen so that all three are in a mutual steady state.

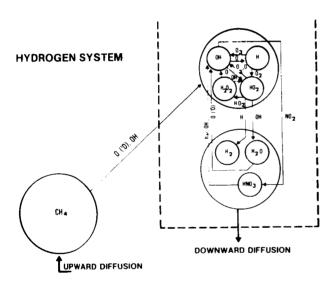


Figure 2

Recombination through  $OH + O_2H \rightarrow H_2O + O_2$  is the principal reaction responsible for depletion of the radicals, resulting in the formation of water, most of which flows downward out of the stratosphere. The balance between  $HO_x$  and  $H_2O$  is established by the reaction between  $O(^1D)$  and  $H_2O$  which recycles hydrogen back into the radical system. Molecular hydrogen, produced in the conversion of  $CH_4$  to  $CO_2$  (McElroy, 1975) and by the reaction

$$H + HO_2 \rightarrow H_2 + O_2$$

and removed by reaction with O(1D)

$$H_2 + O(^1D) \rightarrow OH + H$$

completes the source-radical-sink chain for the hydrogen system.

The Nitrogen System

Figure 3 is an analogous schematic for the stratospheric nitrogen system, which is fed ultimately by bacterial fixation of nitrogen (Alexander, 1971) resulting in the production of  $N_2O$  which diffuses upward through the troposphere. Reaction with  $O(^1D)$  above the troposphere (Bates and Hays, 1967; McElroy et al., 1976).

$$N_2 O + O(^1D) \rightarrow N_2 + O_2$$
  
  $\rightarrow NO + NO$ 

initiates the  $NO_x$  system consisting principally of NO and  $NO_2$ . The reaction of  $NO_2$  with the hydroxyl radical

$$OH + NO_2 + M \rightarrow HNO_3 + M$$

forms nitric acid, which is the major sink term. The  $(NO_2 + NO)$ :  $HNO_3$  ratio is established by photolysis of  $HNO_3$  and reaction with OH

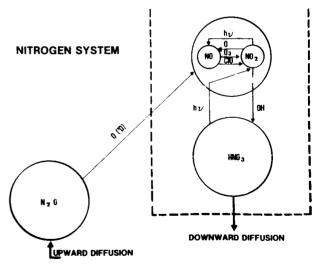


Figure 3

$$HNO_3 + h\nu \rightarrow OH + NO_2$$
 $OH + HNO_3 \rightarrow H_2O + NO_3$ 

balanced by the above recombination step forming  $HNO_3$ .

# The Chlorine System

Figure 4 shows the chlorine system in a similar way, starting with the multiple sources (Rowland and Molina, 1975)  $CCl_4$ ,  $CH_3Cl$ ,  $CF_2Cl_2$  and  $CFCl_3$ , which are photolyzed to yield at least one chlorine atom, which, along with its oxide radical partner ClO, constitutes the basis of the  $ClO_x$  radical system. The chlorine sink term is HCl, which is formed primarily through the reaction of Cl with methane and the perhydroxyl radical

$$CH_4 + Cl \rightarrow HCl + CH_3$$
  
 $HO_2 + Cl \rightarrow HCl + O_2$ 

The ClO<sub>x</sub>: HCl ratio is established by the above two reactions in competition with the recycling step.

$$HC1 + OH \rightarrow H_2O + C1$$

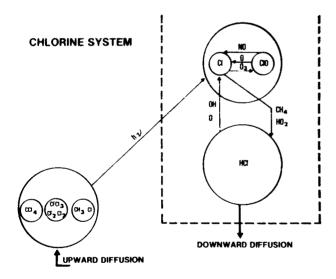


Figure 4

Compounds containing other halogens, e.g., bromine, are thought to behave in a manner similar to that of the chlorine compounds.

An inspection of Figures 1 through 4 shows three key points:

- (1) The radicals form the chemical link between the source and sink terms. Without empirical evidence of their existence and absolute concentration, verification of theoretical calculations relating the source and sink terms remains incomplete.
- (2) The radical species react directly with ozone and atomic oxygen, catalytically recombining the latter two into molecular oxygen and thus establishing the efficiency of the chemical loss process for ozone in the stratosphere.
- (3) The HO<sub>x</sub>, NO<sub>x</sub>, and ClO<sub>x</sub> systems are coupled together such that it is impossible to draw quantitative conclusions regarding the relative effect of any one system upon ozone without simultaneous knowledge of the others.

The last fact becomes extremely important in the consideration of plans for stratospheric measurements.

Requirements: Accurate chemical rate data for the reactions shown in Figures 2, 3, and 4.

Stratospheric measurements of one or more radicals in each of the major chemical systems, especially OH, O, and O(<sup>1</sup>D), which play major roles in each system. Simultaneous measurements are preferred in order to understand the coupling between the systems.

Measurements of the source and sink terms in the  $HO_x$ ,  $NO_x$ , and  $ClO_x$  systems.

There are other species in the stratosphere that have only small effects on ozone concentration, usually indirectly, but which could have major effects on other properties of the stratosphere, like the absorption and transmission of radiation. In this category are the oxides of carbon, oxides of sulfur and sulfate aerosols, particulate matter, hydrocarbons, and charged particles.

#### Oxides of Carbon

Carbon dioxide (CO<sub>2</sub>) plays an important role in determining the temperature of the Earth. It absorbs solar radiation throughout the spectral region, but is primarily an absorber and emitter of radiation in the infrared (IR) region. By absorbing IR radiation emitted by the Earth's surface and reradiating it to space and back toward the Earth, CO<sub>2</sub> helps to cool the upper atmosphere and to warm the lower atmosphere. Because CO<sub>2</sub> does not appear to be very reactive in the stratosphere and is not photodissociated to a significant extent below 80 km, there is very little global variation

in its mixing ratio. This fact has made CO<sub>2</sub> very useful in determining temperature profiles and local and global radiation balance.

Carbon monoxide seems to have very little impact in the stratosphere. Its major source is in the troposphere, although it is a byproduct of methane oxidation in the stratosphere. Its concentration has been found to decrease rapidly above the tropopause (Seiler and Warneck, 1972). The reaction of CO with OH is well known and through such a reaction CO could have some indirect influence on ozone concentration in the stratosphere.

Requirements: Measurement of temperature profiles by observation of CO<sub>2</sub> emissions.

Measurement of CO profiles to indirectly corroborate OH measurements.

# The Sulfur System

The main effect of sulfur compounds in the stratosphere is through the formation of sulfate aerosols. The aerosols, in turn, cause perturbations in the transmitted solar radiation at the tropopause as a consequence of backscattering (i.e., albedo) and absorption. The latter perturbations are postulated to cause corresponding temperature perturbations at the Earth's surface. The system is shown in Figure 5. The sulfur sources are in the troposphere, principally in the form of sulfur dioxide  $(SO_2)$ , with small contributions from hydrogen sulfide  $(H_2S)$  and dimethyl sulfide,  $(CH_3)_2S$ . Approximately

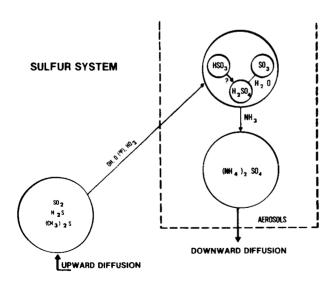


Figure 5

two-thirds of the tropospheric sulfur comes from natural sources in the form of inorganic and organic sulfides. These sulfides are typically oxidized to SO<sub>2</sub> within days. The other third comes from anthropogenic sources through the burning of sulfur-containing fossil fuels.

The complete mechanism for converting  $SO_2$  to aerosols is not yet fully understood. Initial reactions with OH

$$OH + SO_2 + M \rightarrow HSO_3 + M$$

with O

$$O + SO_2 + M \rightarrow SO_3 + M$$

and with HO<sub>2</sub>

$$HO_2 + SO_2 \rightarrow SO_3 + OH$$

have been postulated with the OH reaction being the most important (Castleman et al., 1974; Davis, 1975). The steps in the conversion of the free radical HSO<sub>3</sub> to  $H_2SO_4$  are not well known, but are presumed to involve both OH and NO (Davis, 1975). The hydrolysis of  $SO_3$  to  $H_2SO_4$  is well established so the only question is whether  $SO_3$  is initially formed from  $SO_2$  via the O and  $HO_2$  reactions. The final step in the aerosol formation reaction with  $NH_3$  or other reactants is straightforward and has been verified in laboratory experiments.

In the stratosphere, there is a relatively uniform region of aerosol particles, typically 0.1 to  $10 \,\mu m$  radius, in concentrations of the order of  $10^6 \,/m^3$  in the altitude range 15 to 20 km. This is the Junge layer, which is believed to be composed principally of sulfate aerosols. The number density of the particles decreases with increasing size, and the particles apparently are in the liquid state (supercooled).

Besides affecting the solar radiation in the stratosphere, the stratospheric aerosols can interact with stratospheric gases in several ways: (a) gas-to-particle conversion processes that introduce new aerosols, (b) physical absorption processes where the aerosols provide catalytic surfaces leading to enhanced reactivity of the gaseous species, and (c) chemisorption processes where the surface of the aerosol may act as a sink for gaseous species.

There are other particulates in the stratosphere besides the sulfate aerosols. Recent measurements (Ferry and Lem, 1974) show that most of the non-sulfate particles in the lower stratosphere are aluminum oxide,  $Al_2O_3$ , presumably from rockets that use solid propellants containing metallic aluminum. Evidence to date indicates that extraterrestrial material, such as meteors

and meteorites, is not an important source of stratospheric particles.

Requirements: A better understanding of the conversion of  $SO_2$  to  $H_2SO_4$ .

More data on stratospheric aerosol composition with special reference to carbonaceous material and trace metals.

More data on aerosol size distribution.

More data on aerosol number density vs. altitude in the stratosphere.

Information on the optical characteristics of aerosols.

Information on the nature of aerosol surfaces.

Better understanding of the nature of heterogeneous reactions in the stratosphere with particular emphasis on surface catalysis of gas-phase reactions.

# Hydrocarbons

The participation of methane in the hydrogen system is shown in Figure 2. Other hydrocarbons, (HC), in sufficient quantities could play a role in the chemistry of the stratosphere. It is known from tropospheric studies of smog formation in cities like Los Angeles, that (HC) participate in complex reaction schemes involving  $NO_{\chi}$  and  $HO_{\chi}$  to produce  $O_3$ . These types of reactions could take place in the stratosphere, especially if the stratosphere is contaminated by effluents from high-flying aircraft. Laboratory studies have shown that free radicals and excited species play roles in the smog-producing reactions involving hydrocarbons. The reactions of the excited species could lead to the formation of very high molecular weight organic compounds that could condense to form aerosols in the stratosphere.

Requirements: Development of methods to measure trace quantities of non-methane hydrocarbons in the stratosphere.

Better understanding of the role of (HC) in tropospheric ozone-forming reactions.

#### Charged Particles (Ions)

Ions appear to affect stratospheric chemistry and physics in two ways: (1) They control the electrical properties, such as conductivity. (2) They attach themselves to stratospheric aerosols, leading to changes in the reactivity of the aerosol with trace gases.

The ion density in the stratosphere is in the range of  $10^2$  to  $10^3$  ions/cm<sup>3</sup>. The ions are divided into groups according to size: electrons, small cluster ions, intermediate ions, and large ions. As the number of electrons is relatively small, there are approximately equal numbers of positive and negative ions.

The production of ionization in the stratosphere is by cosmic rays, which in addition to electrons, produce positive ions in proportion to the ambient neutral species, N<sub>2</sub> and O<sub>2</sub>. The electrons rapidly attach to molecules, and the resultant ions have been found to form complex clusters with water molecules (Narcisi, 1973). Cosmic rays are also believed to result in a significant amount of nitric oxide in the stratosphere although the global rate of production from this mechanism appears to be small compared with that from nitrous oxide (Brasseur and Nicolet, 1973).

The most important ion-loss process is recombination (mutual neutralization). The overall electrical properties of the stratosphere appear to be dominated by the small-ion effects, provided that the concentration of small ions is greater than that of electrons by a factor of 10<sup>4</sup> or more (Cole and Pierce, 1965).

Requirements: Laboratory measurements of ion mobilities.

Measurement of ion vertical profiles in the stratosphere.

More data on effects of charged particles on the surfaces of aerosols (particulates).

Better understanding of the processes whereby large cluster ions are thought to grow into or attach to aerosols.

#### Stratospheric Dynamics

Stratospheric motions occur on different space and time scales. The stratospheric motions that control the movement of species from one region to another can be classified as (1) vertical transport (2) meridional circulation (3) zonal circulation (4) very large scale eddy motions and (5) synoptic-scale eddy motions and mesoscale motions.

#### Vertical Transport

An investigation of the mechanisms by which material moves into and out of the stratosphere is extremely important in any long-term study of that region. The dearth of information forces theoreticians, in predicting the effects of pollutants in the stratosphere, to adopt the "eddy-diffusion coefficient" approach in which the

motion is assumed to be vertical and time-independent. The continuity equation can be written as:

$$\frac{\mathrm{d}}{\mathrm{d}z}\left[K(z)N(z)\right]\frac{\mathrm{d}f}{\mathrm{d}z}=\left[P-L\right]$$

where z is height, K(z) is an effective diffusion coefficient (cm<sup>2</sup> s<sup>-1</sup>), N(z) is total density at z, f is the mixing ratio of the trace constituent, and P and L are production and loss rates, respectively. Different theoreticians choose different values for the coefficient K, which accounts in part for the difference in predictions about stratospheric pollution. One method, (Wofsy and McElroy, 1973) is to select the value of K that reproduces the observed vertical profiles of CH<sub>4</sub>, CO, and N<sub>2</sub>O.

A second method, (Johnston et al., 1974) is to choose K to reproduce the measured vertical profile of compounds containing carbon-14 in the stratosphere, the compounds being remnants of the nuclear bomb testing in the atmosphere. There is reasonable agreement between the two methods.

The long-term study of transport processes across the tropopause and mesopause is to be a part of the basic science program. Attempts will be made to utilize theoretical calculations and remote-sensing instrumentation to study the actual fluid physics of the regions.

#### Meridional Circulation

The meridional circulation as given by the zonal averages of the north-south and vertical motions is very difficult to observe directly. The circulation is generally inferred from the balance requirements in the dynamic and thermodynamic equations of the stratospheric models (Mahlman, 1969). The winter meridional circulation in the stratosphere generally consists of two cells: rising motions over the Equator and at high latitudes, and a sinking motion in middle latitudes.

The stratospheric meridional cells play a role analogous to the tropospheric cells in keeping the zonal winds in thermal wind balance with the zonal temperature field, in the presence of sources of zonal momentum or heat (including the sources due to eddy transport convergence) and frictional or radiative damping. In terms of climatic impact, this means that, even if the heating rates due to some physical process are known, such as stratospheric aerosols emitted from a volcanic eruption, it is not possible to infer the magnitude of the temperature change without a dynamic model calculation because there would be no way to determine how much of the heating is balanced by

adiabatic cooling through vertical motions. The dynamic constraints in equatorial latitudes require production of zonal available potential energy in the thermal field to be accompanied by a much greater generation of zonal kinetic enegy. Simply put, it may be easier to produce a temperature perturbation with a momentum source than with a thermal source (CIAP Monograph I, 1975).

#### Zonal Circulation

In the stratosphere, the zonal circulation is mostly from the west in winter and from the east in summer, with maximum values in middle latitudes near the stratopause. In addition to the reversal of sign from summer to winter, there is a departure from zonal symmetry which is larger in winter than in summer. This departure is believed to be the consequence of tropospheric disturbances. In general, the zonal circulation in the stratosphere is greatly influenced by waves propogating vertically upward from the equatorial troposphere (Kousky and Wallace, 1971).

# Large-Scale Eddy Motions

The large-scale eddy motions are usually referred to as planetary waves, since they produce asymmetries in the stratospheric circulation patterns that are planetary in scale. Large eddy transports occur in the presence of these waves, but these transports are very poorly parameterized by an eddy-diffusion theory. However, these eddies do represent a major mechanism for exchange of momentum and eddy-energy between the troposphere and stratosphere. Their existence forms the basis for the "eddy-diffusion coefficient" approach discussed previously.

The large-scale eddies are believed to be the mechanism by which "sudden warmings" occur in the stratosphere. Sudden warmings indicate a breakdown of the winter stratospheric zonal flow. An explanation of the phenomenon has been given by *Matsuno* (1971). He showed how a sudden increase of wave motion in the troposphere can produce a transient, vertically propagating planetary wave, which by transporting potential vorticity southward destroys the stratospheric westerlies and warms polar latitudes.

The variability of the eddy motions is larger in the stratosphere, as compared with that of the troposphere. Even averaging over a winter, the eddy momentum transport fluctuates considerably from year to year making it even more difficult to represent the vertical motion by a single diffusion coefficient.

The synoptic scale refers to horizontal scales of a few hundred to a few thousand kilometers. Motions on this scale are controlled largely by the properties of nonlinear hydrodynamic flow, and simple wave theory does not accurately describe their behavior. The synopticscale motions are important for the eddy flow in the lower stratosphere, i.e., below 15-km where the topside of synoptic-scale tropospheric eddies is greater in amplitude than the planetary-scale waves. The concept of potential vorticity becomes very useful for the interpretation of the synoptic-scale motions of the lower stratosphere. It not only serves as a tracer of motions. but also generates the time evolution of the flow. Synoptic-scale eddies in the lower stratosphere serve the very important role of regulating total ozone content by transporting ozone poleward and downward, ultimately across the tropopause to destruction in the troposphere (Danielsen, 1968).

On the mesoscale, orographically induced gravity waves and clear-air turbulence are of frequent occurrence in the lower stratosphere. The importance of motions on this scale for transport processes is in their irreversible mixing of air and consequent destruction of potential vorticity.

Requirements: Development of better methods to study small scale dynamics including tropospheric-stratospheric exchanges.

Improvement in tracer studies of large scale stratospheric motions.

More observations of stratospheric dynamic processes such as "warmings."

Development of better dynamic models.

# SHORT-TERM ASSESSMENT PROGRAM

While the information is being obtained to develop an organized body of knowledge of the physics, chemistry and transport processes occurring in the upper atmosphere, it has become necessary to make current assessments of the effects of certain identified actions by man that could cause severe perturbations in the stratosphere, especially on ozone. These man-generated actions include: (1) Space Shuttle operations in the stratosphere, (2) the release of chlorofluoromethanes (CFM's, used in aerosol spray cans, as foaming agents and as refrigerants) that diffuse into the stratosphere, and (3) aircraft flights in the upper troposphere and the lower stratosphere.

The assessment of these actions is distinguished somewhat from the long-range program by the relatively short

time (3 to 5 years) in which the effects must be analyzed and by the narrow concentration on specific perturbations to the normal physics and chemistry of the upper atmosphere. The short-term program can be viewed as a subset of the broader, more general, long-range program.

The approach used in making the short-term assessments is to (a) gather the pertinent data, making new measurements as feasible, (b) use these data in existing mathematical models to predict future effects, (c) evaluate and compare results with the original hypothesis that led to the concern, and (d) recommend corrective action, if warranted. The end product in each of the assessments is a report for use by appropriate authorities in their decision-making procedures.

# **Aircraft Operations**

The hypothesis is that large fleets of subsonic and supersonic aircraft flying in or just below the stratosphere emit oxides of nitrogen  $(NO_x)$  and sulfur  $(SO_x)$  that could adversely affect the ozone level and solar radiation transmission in the stratosphere. To test this hypothesis, it is necessary to develop data on (a) background concentrations of  $NO_x$  and particulate matter in the stratosphere, (b) their chemical reactions with other chemical species, and (c) all sources and sinks of  $NO_x$  in the atmosphere.

Much data on this topic were obtained during CIAP and published in a series of monographs (CIAP, 1975). These data were reviewed by the National Academy of Sciences (NAS) through its Climatic Impact Committee (CIC). The CIC issued a report (Climatic Impact 1975), summarizing Committee, its findings. It concluded that the original hypothesis appears to be valid and there is reason for concern. The DOT through Federal Aviation Administration (FAA) has developed a new program, the High Altitude Pollution Program (HAPP) to continue to investigate aircraft pollution. The objective of HAPP is "to quantitatively determine the requirements for reduced cruise altitude exhaust emissions and, in conjunction with the Environmental Protection Agency (EPA) and the International Civil Aviation Organization (ICAO), to ensure that, as necessary, appropriate regulatory action is taken to avoid environmental degradation" (HAPP, 1975). HAPP will continue to obtain data on NO<sub>x</sub> and particulate

NASA's assessment of aircraft operations is complementary to HAPP. NASA's role is to determine baseline data on the interaction of exhaust emission products and minor constituents in the stratosphere. This is accomplished primarily through the Global Atmospheric Sampling Program (GASP), a program started by NASA

in 1972 to equip commercial 747 jet aircraft to measure NO, CO,  $O_3$ ,  $H_2O$  and particulates. It is planned to use data from this program, as well as data from other NASA programs studying aircraft emissions, in making the aircraft assessment. The FAA and other Federal agencies will be given the baseline data along with the assessment report to aid them in making their own assessments and recommendations for corrective actions.

# **Space Shuttle Operations**

The original hypothesis was that the exhaust products from the planned 60 Space Shuttle launches per year by 1983 would lead to a significant reduction in stratospheric ozone concentration. This was the prediction of some of the scientists invited to a meeting at the Kennedy Space Center (KSC) in February 1974 to discuss the environmental impact of Space Shuttle operations. At that time, a program was initiated to test the hypothesis through a coordinated effort of field measurements, laboratory experiments, and theoretical studies. The emphasis was on the two exhaust products of the Solid Rocket Motors (SRMs), HCl and Al<sub>2</sub>O<sub>3</sub>.

# Hydrogen Chloride

Hydrogen chloride is converted to active chlorine atoms by reactions with OH, O, and by photo-dissociation.

$$HCl + OH \rightarrow H_2O + Cl$$
  
 $HCl + O \rightarrow Cl + OH$   
 $HCl + h\nu \rightarrow Cl + H$ 

The chlorine atoms can then participate in reactions with ozone according to the scheme in Figure 4.

At the time of the Kennedy Space Center (KSC) meeting, the prevailing opinion was that ambient stratospheric concentrations of chlorine-containing compounds were too small to be measured by existing instrumentation or by any technique being proposed for the near future (3 to 5 years). Thus, the decision was made to concentrate on the measurements of hydroxyl radicals and oxygen atoms in the stratosphere in order to assess the effects of HCl. The capability did exist, in the laboratory, to measure chlorine atom reactions and hydroxyl reactions. A set of chemical reactions as shown in Table 1 was selected for further study.

Reaction 2 in Table 1 is important in that it is the primary reaction that converts reactive Cl to the less reactive HCl. This reaction is viewed as a temporary sink for active chlorine; temporary because HCl can be rapidly converted back to Cl by reactions (4) and (5).

Table 1. Reactions<sup>a</sup> selected for study in Space Shuttle assessment

(1)	CI	+	$O_3$	$\rightarrow$	CIO	+	$O_2$
(2)	CI	+	CH₄	$\rightarrow$	HCI	+	$CH_3$
(3)	Cl	+	$H_2$	$\rightarrow$	HCI	+	Н
(4)	HCI	+	ОН	$\rightarrow$	$H_2O$	+	CI
(5)	HCI	+	0	$\rightarrow$	CI	+	ОН
(6)	CIO	+	0	$\rightarrow$	CI	+	$O_2$
(7)	CIO	+	NO	$\rightarrow$	CI	+	$NO_2$
(8)	CIO	+	O <sub>3</sub>	$\rightarrow$	?		

<sup>a</sup>At the time of the KSC Meeting, reactions involving chlorine nitrate (CINO<sub>3</sub>) were not identified as being important. Thus, they are not included in the table.

Reaction (7) is important since it affords an alternate path for ClO to be converted to Cl. Taken with the reaction,

$$NO_2 + h\nu \rightarrow NO + O$$

the results yield no net destruction of ozone. Reaction (7) also shows the coupling between the  $NO_X$  system and the  $CIO_X$  system.

When the existing data on the key chemical reactions were fed into previously developed one-dimensional mathematical models of the stratosphere (at Harvard by McElroy, at Ames Research Center by Whitten, and at Michigan by Cicerone and Stolarski), the results indicated that 60 Space Shuttle launches per year would lead to an ozone reduction of 0.44 percent, with a factor of 6 uncertainty on the high side and a factor of 10 on the low side. The large uncertainties occurred primarily because of the lack of information on the OH concentration in the stratosphere. The factor of 6 represented the maximum amount of OH needed to convert all of the HCl from the SRMs to Cl.

Since the KSC meeting, measurements have been made of atomic oxygen (O) and hydroxyl (OH) in the stratosphere; improved laboratory measurements have been made concerning reactions (1) and (2); the mathematical one-dimensional models have been improved; there is now general agreement among the models in predicting observable stratospheric conditions (Shimazaki and Whitten, 1976).

When the new data are fed into the improved onedimensional models, the predicted ozone reduction from continuously launching 60 Space Shuttles a year is 0.2 percent with a factor of 3 uncertainty.

# Aluminum Oxide

The concern about  $Al_2O_3$  particles centers around their ability to affect the radiative transfer processes in the upper atmosphere by serving as scattering centers for solar radiation. It is also postulated that they could provide active sites on their surfaces for chemical reactions to take place. Both of these possibilities have been investigated and it is now believed that the potential is negligible for  $Al_2O_3$  from Space Shuttle operations to affect the stratosphere.

# Chlorofluoromethanes

In 1974, Molina and Rowland (1974) postulated that the chlorofluoromethanes F-11 (CF<sub>3</sub>Cl) and F-12 (CF<sub>2</sub>Cl<sub>2</sub>) were being transported into the stratosphere and dissociated by ultraviolet light. One of the dissociation products is chlorine atom, which can participate in the catalytic destruction of ozone as shown in Figure 4. The CFMs are known to be photo-dissociated by electromagnetic radiation in the far ultraviolet, below 225 nm. In the stratosphere, the CFMs are decomposed only by radiation in the relatively narrow band between 184- and 225-nm region.

The bond dissociation energy for the C-Cl bond in the CFMs is about 70 to 75 kcal/mole. This means that dissociation could occur with absorbed light at any wavelength shorter than about 500 nm. However, absorption is observed only in the far ultraviolet where the energy is far in excess of the minimum required for breaking the C-Cl bond. The photochemical process is assumed to be a transition (n-\u03b3) involving excitation to a repulsive electronic state that immediately dissociates, breaking the C-Cl bond. The C-F bond in the CFMs is much stronger (110 to 130 kcal/mole), and the available energy in the absorption region is actually sufficient for dissociation of the C-F bond. This could lead to the formation of HF in the stratosphere.

Some work has been performed on the photodissociation of CFCl<sub>3</sub> and CF<sub>2</sub>Cl<sub>2</sub> (Rowland and Molina, 1975, Doucet, 1973). Molina and Rowland (1974) found photodissociation rates, globally averaged for diurnal and zenith angle effects, to be about  $0.34 \times 10^{-7} \, \mathrm{s}^{-1}$  at 30 km and about  $0.51 \times 10^{-9} \, \mathrm{s}^{-1}$  at 20 km for the CFMs. They calculated the peak in the destruction rate to be about 30 km, which leads to an altitude profile for released Cl atoms similar to that for the initial formation of ozone, although relatively reduced at the upper edge of the ozone formation region.

Theoreticians using available data, primarily from laboratory experiments, have predicted long-term effects of the CFMs on stratospheric ozone. Cicerone, et. al., (1974) along with Wofsy et al., (1974) showed that the current CFM usage levels and trends could lead to chlorine-catalyzed  $O_3$  destruction rates that would exceed all natural sinks of stratospheric  $O_3$  by the early 1980's. Wofsy et al. showed that continuous use of the CFMs at the 1972-73 growth rate could lead to a very large ozone reduction ( $\sim$  25%) by the year 2000. The predictions formed the basis for the original IMOS concerns.

In the NASA program, specific field measurements are being conducted to:

- (1) Measure the vertical profiles from the upper troposphere to the upper stratosphere to determine whether the CFMs are:
  - (a) reaching the stratosphere in the amounts predicted.
  - (b) being photodissociated into Cl atoms above 30 km at the predicted rates.
- (2) Determine the vertical profiles of HCl to study sinks for chlorine compounds.
- (3) Determine the concentrations of the products of photodissociation, chlorine atoms, and their reaction product with ozone, chlorine monixide (CIO).
- (4) Measure fluorine compounds such as HF and CF<sub>2</sub>O, both postulated to be final products of the photodissociation.

Laboratory experiments are being conducted to obtain the rate data for many of the chlorine reactions identified in the Space Shuttle assessment as well as for those involving the CFMs themselves.

The results of the NASA program will be coordinated with those from other Federal agencies investigating the effects of the CFMs.

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# IV. PROGRAM IMPLEMENTATION

The Director of the Upper Atmospheric Research Office (UARO) has the overall responsibility for implementation of the program. He reports to the Associate Administrator for Space Science who is responsible for seeing that the program is coordinated with related NASA programs and with the programs in other Federal agencies. The Associate Administrator for Space Science is expected to work with interagency committees, such as ICAS, to ensure proper coordination among the Federal programs.

The data needed to satisfy the requirements of the basic science program and for making the short-term assessments will be obtained from a coordinated effort of field measurements, laboratory experiments, and theoretical studies. In the long-term program, these efforts will be tightly coupled and complementary to each other. For example, data from the field measurements will not only be used to provide fundamental information about the concentration of stratospheric species, but will also be used in the theoretical studies in model development and validation. Conversely, model predictions will be checked and tested through field measurement and laboratory experiments. In the laboratory studies of reaction rates, the emphasis will be on those chemical reactions that have been identified in the modeling efforts as being important to the understanding of stratospheric behavior. However, new important reactions are expected to be discovered during laboratory investigations; these will be considered in the modeling efforts.

#### FIELD MEASUREMENTS

As the data obtained from the field measurements will be used for model development and validation, one long-term objective is to establish an effective and rational field measurements program. Initially, the program must stress in situ measurements, since existing remote instruments cannot make all of the stratospheric measurements to understand stratospheric composition and behavior. Eventually, as our understanding of stratospheric processes improves, and the development of remote-sensing instruments progresses, remote methods will replace some or all of the in situ methods. However, because remote measurements are obviously limited to

those parameters that can be sensed from a distance, there will be a continuing need for comparison with more direct measurements. In the NASA Program, field measurements will be used to obtain the data necessary to satisfy the stated requirements in the long-range program. These measurements will include:

- (1) Determination of atomic oxygen concentration in the stratosphere.
- (2) Monitoring of solar radiation.
- (3) Monitoring ozone on a global scale.
- (4) Measurement of those identified species in the HO<sub>x</sub>, NO<sub>x</sub>, and ClO<sub>x</sub> systems that strongly influence ozone concentrations.
- (5) Determination of stratospheric temperatures by measuring CO<sub>2</sub> radiation.
- (6) Determination of stratospheric circulation.
- (7) Determination of aerosol size distribution, composition, and number density.
- (8) Determination of hydrocarbon concentration in the stratosphere.
- (9) Determination of ion composition and vertical profiles in the stratosphere of minor constituents.

Ideally, these measurements should be made simultaneously in space and time in order to fully understand the physics and chemistry of the stratosphere. Unfortunately, the necessary instrumentation and measuring techniques do not exist at the present time to accomplish this task. However, simultaneous measurements remain one of the ultimate objectives of the field measurements program.

#### **Development of Platforms**

Platforms must be provided for the instrumentation needed for any field measurement effort. NASA has investigated the long-term use of measurement platforms in stratospheric research. The report Measurement Platforms for Stratospheric Research, soon to be published as a supplement to the NASA Program on Upper Atmospheric Research, addresses the role of aircraft,

balloons, sounding rockets, and satellites, as well as the use of parachutes and ground-based instrumentation, in the measurement program.

Each platform has its own unique capabilities. Satellites have the obvious advantage of being able to provide global coverage within a 1-day period, good and somewhat flexible sampling characteristics, and low cost per datum obtained. Sounding rockets can provide access to those altitudes beyond the capability of aircraft and balloons and below the regions normally penetrated by satellites. Balloons provide a very stable, vibration-free platform that can ascend or descend through the stratosphere carrying either in situ or remote sensing instruments for vertical profile measurements. Aircraft have a relatively short lead time and larger weight capability than can be achieved currently with satellites and also have the ability to cover-large geographic areas in a time period short in comparison to balloon measurements.

Ground-based instruments also have a role in stratospheric measurements. NOAA operates an extensive ground-based network where many of the stratospheric species are measured, including CO<sub>2</sub>, O<sub>3</sub> (total column content), and aerosols. Some of the stations are also equipped to measure NO<sub>x</sub>, SO<sub>2</sub> and solar radiation. It is possible to use ground-based instruments to measure some of the reactive stratospheric species such as OH (Burnett, 1976). A ground-based method for measuring CIO is being tested by radio astronomers utilizing the telescopes designed for astronomical investigations.

Eventually, the data obtained from the field measurements, along with necessary support from laboratory experiements and modeling, will be used to design and establish a global monitoring program that could provide a basis for environmental control.

#### **Global Monitoring Requirements**

By its very nature, a global stratospheric monitoring system will depend in large part on satellites to provide the quasi-synoptic repetitive coverage needed for identification and tracking of the concentration, transport, and disposition of the trace constituents which are believed to have a significant influence on the Earth's ozone shield and on climate. In such a system, ground-based stations, provided they are further developed, could give 24-hour coverage at specified locations. The existing ground-based stations provide the most reliable data and could, through improved technology, give extensive diumal coverage of stratospheric processes.

Within NASA, the responsibility for developing the technology needed for a global monitoring system is in the Office of Applications (OA). The OA-planned pro-

gram in this area involves the development of a comprehensive measurements technology based on remote sensing techniques. The OA program supports the following objectives:

- (1) Sensor Development: Development of remote sensors for measuring the concentrations, distributions, and dynamics of minor atmospheric constituents and temperature from satellites, aircraft, sounding rockets and balloons.
- (2) Data Analysis: Analysis of sufficient data for evaluations of the performance of sensor systems and their usefulness in monitoring; this includes a continuing analysis of Nimbus 4 BUV global ozone data.
- (3) Modeling: Participation in the development of numerical atmospheric models simulating the large scale dynamic, chemical, and radiation processes of the atmosphere for studying the global or regional environmental effects of pollution and its impact on climate.
- (4) Other Sampling Support: High-altitude aircraft, sounding rocket, and balloon measurements to provide for initial test of sensors, data upon which to base sensor design, a means for calibration of research and global monitoring sensors, and a compositional benchmark to assist in the analysis of remote sensor data. In situ sensors will also be developed and flown to help establish the specification criteria for remote sensor development.

Ozone must be the major candidate in any global monitoring system and should be monitored preferably from both ground-based stations and from satellites for several multiples of the 11-year solar cycle with correlated measurements of solar ultraviolet radiation (especially 200 to 220 nm). It is necessary to monitor the various chemicals that form the sources and sinks in the hydrogen, nitrogen, chlorine and sulfur systems and as many of the radical species as possible. For the first 5 or 10 years of the program, there should be sufficient monitoring of enough of these species to establish or confirm cause-and-effect relations. Later the species monitored for surveillance or control might be reduced in number. It may be that measurements of O<sub>3</sub>, solar far ultraviolet, NO<sub>2</sub>, N<sub>2</sub>O, H<sub>2</sub>O, SO<sub>2</sub>, HCl, and organic chlorides will be sufficient for use in any control strategy.

Aerosols, ions, and hydrocarbons are other stratospheric species that should be measured from a global monitoring system, although no means for remotely measuring ions and stratospheric hydrocarbons have been identified at present.

Table 2 lists those species that are being investigated in the current field measurement program along with the measurement technique, platform, and investigator. Also included are the proposed experiments on Nimbus G, a satellite to be launched in 1978, and on the Stratospheric Aerosol and Gas Experiment (SAGE) to be launched in 1979. During the periodic update of the program document, the list of species in Table 2 is

expected to change, with new species being added as they become identified and necessary instrumentation becomes available. A complete listing of all the tasks in the current NASA Program is given in the Appendix.

An examination of Table 2 shows some of the future needs in field measurements. These include, instrumentation and measuring techniques for  $O(^1D)$  and  $O_2(^1\Delta)$ ;  $HO_2$ ; and  $NH_3$  and  $NH_4^+$ .

Additional measurement techniques are necessary for Cl, ClO, and OH because of the importance of these species in stratospheric chemistry.

Table 2. Current Program in Field Measurements

Species	Method	Platforms	Investigator	
CI, CIO	Resonance Fluorescence	Balloon	Anderson/Stedman	
CIO	Infrared Spectroscopy	Aircraft, Balloon	Farmer	
	Filter Capture	Aircraft, Balloon	Lazrus	
	Millimeter Spectroscopy	Aircraft	Waters	
	Millimeter Spectroscopy	Ground-based	Stokes	
	Ultraviolet Spectroscopy	Ground-based	Nicholls	
HCI	Infrared Spectroscopy	Aircraft, Balloon	Farmer	
	Filter Capture	Aircraft, Balloon	Lazrus	
CFCI <sub>3</sub> , CF <sub>2</sub> CI <sub>2</sub>	Grab, Cryo-sample	Aircraft, Balloon	Arvesen	
	Grab Sample	Aircraft	Rasmussen	
ОН	Resonance Fluorescence	Balloon	Anderson	
	Laser Fluorescence	Aircraft	Wang	
0	Resonance Fluorescence	Balloon	Anderson	
CH₄	Grab Sample	Aircraft, Balloon	Loewenstein	
HBr, Bro, Br	Filter Capture	Aircraft, Balloon	Lazrus	
CH <sub>3</sub> Br	Cryo Sampler	Aircraft, Balloon	Arvesen	
NO	Chemiluminescence	Balloon	Schiff	
NO, NO <sub>2</sub> , HNO <sub>3</sub>	Chemiluminescence	Aircraft	Loewenstein	
HNO <sub>3</sub>	Filter Capture	Aircraft, Balloon	Lazrus	
N, O	Grab Sample	Aircraft	Rasmussen	
Aerosols	Impact	Aircraft	Ferry	
Aerosois	Photometer (Solar)	Satellite	Pepin	
O <sub>3</sub>	Ultraviolet (BUV)	Satellite (Nimbus 4, AE-E)	Heath	
Temperature (CO <sub>2</sub> )	Radiometry (HIRS)	Satellite (Nimbus 6)	Smith	
Temperature	Radiometry (PMR)	Satellite (Nimbus 6)	Houghton	
Solar Flux	Radiometry (ERB)	Satellite (Nimbus 6)	Jacobowitz	
O,, H, O, T	Radiometry (LRIR)	Satellite (Nimbus 6)	Gille	

Future Satellite Systems					
0,	Ultraviolet (SBUV/TOMS)	Nimbus G (1978)	Heath		
O <sub>3</sub> , HNO <sub>3</sub> , NO <sub>2</sub> , H <sub>2</sub> O, T	Radiometry (LIMS)	Nimbus G (1978)	Russell/Gille		
H <sub>2</sub> O, N <sub>2</sub> O, CH <sub>4</sub> , CO, NO	Radiometry (SAMS)	Nimbus G (1978)	Houghton		
Aerosois	Photometry (SAM II)	Nimbus G (1978)	McCormick		
Solar Flux	Radiometry (ERB)	Nimbus G (1978)	Jacobowitz		
O <sub>3</sub> , Aerosols	Photometry	SAGE, 1979	McCormick		

For the long-term field measurement program, other identifiable future needs are:

- (1) Development of remote instrumentation to simultaneously measure as many of the stratospheric parameters as possible including solar radiation, radicals in the HO<sub>x</sub>, NO<sub>x</sub>, and ClO<sub>x</sub> systems, hydrocarbons, ions, aerosols, stratospheric temperatures, and stratospheric winds.
- (2) Expansion of in situ methods to include the simultaneous measurements of chemical sources and sinks in each of the major stratospheric systems.
- (3) Development of methods to measure hydrocarbons in the stratosphere.
- (4) Improvement of the instrumentation needed to measure ions in the stratosphere.
- (5) Development of a global monitoring network using all available measurement platforms but concentrating on ground-based and satellite systems.

#### LABORATORY EXPERIMENTS

In the long-range program, laboratory experiments will concentrate on:

- Photochemistry, including absorption coefficients, photolysis channels, quantum yields, and some spectroscopy.
- (2) Reaction rates and mechanisms including those leading to sulfate aerosols.
- (3) Optical properties of aerosols.
- (4) Nature of aerosol surfaces including those with positive or negative charges.
- (5) Understanding the role of HCs in tropospheric ozone-forming reactions.
- (6) Determination of ion mobilities and composition.
- (7) Generation of calibration spectra for field instruments.
- (8) Study of heterogeneous reactions.
- (9) Sensor development and measurement techniques.

# Photochemical and Spectral Data

The photochemistry of ozone will obviously be a part of any long-term study of photochemical processes in the stratosphere. There is a need to understand the details of the wavelength and temperature dependence of the reaction

$$O_3 + h\nu \rightarrow O_2 + O(^1D)$$

since it is very important in ozone chemistry in the stratosphere.

A second problem in ozone photochemistry is the possible temperature dependence of the  $O_2$  absorption coefficients in the Herzberg region. If there is a significant temperature dependence, it could drastically change the predictions of ozone reduction in the stratosphere. The temperature dependence of the absorption coefficients of all important species in the stratosphere must and will be carefully examined.

#### Rate Data

For the long-term program, the experiments designed to obtain rate data will address radical-radical reactions and reactions between radicals of one stratospheric species with the neutrals of another. Some examples are:

OH + 
$$HO_2 \rightarrow H_2O + O_2$$
, H +  $HO_2 \rightarrow 2$  OH

$$HO_2 + O \rightarrow OH + O_2$$
,  $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$ 

Sophisticated new techniques such as resonance fluorescence will be further developed to study very reactive species under stratospheric conditions.

Many of the homogeneous gas phase reactions occurring in the stratosphere are already being studied by conventional chemical kinetic techniques and probably will not be a major part of a long-range plan in laboratory experiments.

On the other hand, heterogeneous reactions have not been given sufficient attention and will be included in the long-term program. Heterogeneous reactions are here defined as those in which a particle, solid or liquid, interacts with gaseous species. The interaction may be catalytic, or the substance may be consumed in the reaction. These reactions will be studied in conjunction with the studies on the surfaces of aerosols. All possible heterogeneous processes that could take place in the stratosphere will be investigated.

# Hydrocarbons

The role of hydrocarbons in the formation of tropospheric ozone will be investigated in the laboratory to ascertain whether a similar process could occur in the stratosphere. Temperature and pressure dependence studies will be carried out to simulate stratospheric conditions.

Stratospheric ions cover a wide-range of mobilities. Mobility is defined as the average velocity of ions (m/sec) in an electric field of field strength (V/m). The coarsest separation of the ion mobility spectrum is into the small or cluster ions (mobilities at STP of  $10^{-4}$  m<sup>2</sup>/V sec and sizes of  $r = 7 \times 10^{-4}$  to  $7 \times 10^{-3}$   $\mu$ m) and into large ions (mobilities on the order of  $10^{-7}$  m<sup>2</sup>/V sec and  $r = 10^{-2}$  to  $10^{-1}$   $\mu$ m). The large ions can be formed by attachment of small ions to aerosol particles. As the mobility of an ion is a function of its size, any change in mobility with altitude is of interest as being possibly indicative of a change in ion character.

Ion mobilities are related to small-ion densities and the conductivity of the medium through the equation:

$$\lambda = \lambda_{+} + \lambda_{-} = 2\lambda_{+} = 2nek$$

where  $\lambda$  is the conductivity, n is the density of positive or negative cluster ions (assumed equal) and  $\underline{k}$  is average mobility of the cluster ions. Thus from a laboratory measurement of  $\underline{k}$ , and a field measurement of n, the conductivity,  $\lambda$ , can be determined. The studies should focus on the applicability of the laboratory data to actual stratospheric conditions (Hoppel, 1968, 1970).

# Measurement Techniques

Laboratory work on new measurement techniques should lead to the development of instruments with the high sensitivity necessary for stratospheric measurements. The instrument used to obtain the first measurement of hydroxyl radicals in the stratosphere was based on a technique developed in the laboratory at the University of Pittsburgh to measure fast chemical reactions. Its application to measurements in the stratosphere demonstrates the potential for new sensors being developed in the laboratory.

There are, at present, very limited methods for measurement of several stratospheric constituents at their ambient concentrations in the stratosphere. Among these constituents are OH, HCl, ClO, HF, NH<sub>3</sub>, SO<sub>2</sub>, HC, O, CH<sub>2</sub>, and  $CF_xCl_y$ . Measurement of hydrocarbons may be important in advanced SST studies; HCl, Cl, and ClO measurements are of interest for Space Shuttle environmental impact evaluations, as well as for the assessment of the effects of CFMs. Other important species that can be detected in the stratosphere, but for which instrument improvements are required, include O<sub>3</sub>, NO, NO<sub>2</sub>, and particles.

Table 3 lists some of the laboratory experiments currently being conducted in the NASA program, including reaction kinetics and spectroscopy. Reaction

	Reaction kinetics				Spectroscopy				
(a) HC1	+	0	(g) C)	+	ο,	CIO Spectra	- Cooper (ARC)		
(b) HCI	+	ОН	(h) CIO	+	o Ó		- Nicholls (York		
(c) CH.	+	а	(i) CIO	+	NO	IR Spectra of			
(d)HO.	+	CIO	(i) CIO	+	NO.	Trace Constituents	- Boese (ARC)		
(e) H.	+	CI	(k) CIO	+	0.		Toth (JPL)		
(f) HO.	+	0	(1) CIOO	+	o.	Chlorofluoromethanes	- Molina (UCI)		
	(m	HO.	+ OH		-,		- Moore (USU)		

Investigators, Kauffman, Davis, Demore

(j) deserves special mention. Recently the formation of chlorine nitrate (CINO<sub>3</sub>) from this reaction was identified as having a possibly large effect on predicted ozone reduction percentages as a consequence of chlorofluoromethane releases. This possibility is now being investigated in the NASA program through new laboratory experiments and theoretical studies.

New critical reactions and measurements will be added to Table 3 as they become identified as having a significant role in the stratospheric ozone balance.

The future needs in laboratory experiments are more accurate laboratory data and the development of sophisticated instrumentation to measure reactions like (m) of Table 3 which, at the present, is extremely difficult to measure.

#### THEORETICAL STUDIES

Much of the information necessary for a complete understanding of the physics and chemistry of the stratosphere cannot be obtained from the field measurements and laboratory studies. It is difficult to understand phenomena like large scale dynamics, stratospheric climate and its variability without the aid of mathematical models that attempt to simulate actual stratospheric conditions. For this reason, the long-term program in theoretical studies emphasizes model development and verification.

The theoretical study phase also includes data analysis, the utilization of data obtained from aircraft flights in the troposphere and lower stratosphere (GASP), and the calculation of spectroscopic constants needed in the interpretation of data from the use of spectroscopic techniques in the field measurement and laboratory experiment phases.

# Modeling

In the long-term program, the modeling effort will concentrate on the development and verification of one-, two- and three-dimensional models that simulate stratospheric conditions. Areas that will receive special attention include:

- (1) Development of sub-model elements such as chemistry, composition/diffusion, circulation and radiative transfer.
- (2) Development of efficient numerical methods to minimize computer time and storage requirements.
- (3) Study of requirements imposed by boundary conditions, especially at the lower boundary where there may be a requirement to use data from a model of the troposphere.
- (4) Sensitivity studies to determine the response of the model predictions to the uncertainties in the input values and to the approximations used in developing the model.

These problems, either individually or in various combinations, represent significant impediments to the development of efficient interactive models and long-term climatic models. For example, detailed radiative transfer calculations cannot be made as a routine part of an extensive calculation because of the computer time involved. Thus, it becomes necessary to study the radiative transfer process and develop a parameterized radiative transfer submodel that will produce accurate results with a minimum expenditure of computing time.

# Chemistry Submodels

Development of chemistry submodels requires both better definition and determination of reaction rates of interest and an extensive series of model studies to optimize the means of including the reaction schemes in the models. In order to trade completeness for manageability, models will be compared to determine the sensitivity of the reaction scheme to the elimination of various reactions.

# Composition and Diffusion Submodels

Composition and diffusion submodels are required in order to develop an understanding of the composition of the ambient atmosphere and the manner in which pollutants diffuse through it.

One area that requires extensive model study is stratospheric dynamics and mixing. For example, the proper relationships between vertical and horizontal mixing do not appear to have been established as exemplified by the use of an empirical factor to simulate eddy diffusion. Also, it has not been established how the local turbulence is influenced by the temperature and temperature gradients, Changes in the turbulence could significantly influence the deposition of pollutants in specific layers of the stratosphere.

The development of submodels to handle these problems will greatly enhance our knowledge of stratospheric diffusion processes.

# Atmospheric Circulation

The mean motions of the atmosphere are the subject of atmospheric circulation modeling and have undergone extensive investigations for many years. Models are available from sources such as the National Center for Atmospheric Research (NCAR), the Goddard Institute for Space Studies (GISS), the University of California, Los Angeles (UCLA), and the Geophysical Fluid Dynamics Laboratory (GFDL). NASA will help to support the continuing development and refinement of these models so that they can be effectively used in the studies of stratospheric climate and climate variability.

# Radiative Transfer

Solar radiation has a major influence on atmospheric chemistry and provides the thermal energy needed to drive the atmosphere. Therefore, it is necessary to include radiation in stratospheric models. The development of radiative transfer submodels will support the measurement program by determining the solar input and the absorption and scattering by stratospheric constituents.

Table 4 lists the modeling efforts that are part of the current NASA program. An examination of the table indicates that NASA does not presently support any GCM work in the stratosphere. As indicated previously, NASA will work with other Federal agencies to help to support the continuing development and refinement of GCMs so that they can be effectively used in the study of atmospheric circulation.

Table 4. Theoretical Studies

Dimensions	Modeling Institution	Investigato		
1	ARC	Whitten		
	LaRC	Callis		
	GISS	Stewart		
	Harvard	McElroy		
	Michigan	Cicerone		
2	ARC	Shimazaki		
	Harvard	McElroy		
3	MIT	Prinn*		

<sup>\*</sup>NASA sponsors adaptation to ILLIAC-IV computer at ARC.

# Data Analysis

A serious problem is that of developing efficient data inversion techniques capable of handling large amounts of data and displaying them in an understandable form in a reasonable time frame. Developing efficient algorithms for constructing constituent profiles from the output of the available measurement system will have high priority in the NASA Upper Atmospheric Research Program. Equally important is the development of techniques for translating the measured values into usable inputs for the models which will be used for the assessment functions.

# Calculation of Spectroscopic Constants

As a complement to the laboratory experiments of spectroscopic parameters, a strong program in theoretical calculation of spectroscopic constants will be pursued. The approach is to use numerical and quantum mechanical methods to calculate parameters such as transition probabilities, lifetimes of excited states, and predissociation factors that can be used to interpret laboratory and field spectra.

#### DATA HANDLING PROCEDURES

In an effort such as the NASA Upper Atmospheric Research Program, which is dependent on a strong coupling among the field measurements, laboratory experiments, and theoretical studies (modeling), it is important that data be handled quickly and efficiently. The theoreticians doing the modeling must have quick access to the latest results from the field measurement and laboratory experiment phases. Scientists who perform the measurements must be aware of the latest model predictions so that their measurement program may be modified accordingly.

#### Fast Information Flow

The telephone provides the easiest and fastest flow of information and circumvents the reluctance of most scientists to put into writing their recent findings before they are ready for publication. NASA will continue to use this method in the Upper Atmospheric Research Program. Plans are underway to establish a central location to receive and transmit via telephone the latest experimental results and model predictions emanating from the program.

For a more formal dissemination of data, a newsletter, of the same format as the CIAP newsletter, is being published at frequent intervals and will contain the latest results from all elements of the program. The letter is published jointly with the FAA/HAPP.

# Computer Data Bank

The feasibility of a computerized data bank is being investigated to ensure that changing trends in stratospheric parameters can be readily noted and to provide researchers with timely access to the multiplicity of stratospheric measurements being made. The primary purpose of this data bank would be to specialize in upper atmospheric research and to provide an efficient means of making current data available for immediate use. Included in such a bank would be ground, aircraft, balloon, rocket, and satellite measurements of ozone and other trace gases, particulate matter, ultraviolet radiation, radioactivity, and charged particles, as well as selected data from meteorological soundings. The details of content, format, and policies for use and distribution would be determined in consultation with the scientific community.

# Chemical Rate Data

NASA plans to use the expertise at the National Bureau of Standards (NBS) for the acquisition, evaluation, storage, and dissemination of the latest data on the rates of chemical reactions. NBS has cataloged the latest chemical kinetics data, including data on ion-molecule reactions for CIAP.

NASA plans to work jointly with HAPP in sponsoring the NBS group to produce similar catalogues on chemical reactions important in making assessments of stratospheric aircraft and Space Shuttle flights and of the CFMs and other chemicals. These three methods of data acquisition and handling, (telephone, coupled with the newsletter; computer bank; and NBS) should provide a rapid and smooth flow of information to potential users.

#### ASSESSMENT REPORTS

The scientific output of the assessment will be a number that describes the predicted change in stratospheric ozone as a function of the rate at which a pollutant (mass/time) is injected into the stratosphere. For each of the assessments, the number is modified by the appropriate input parameters such that the final results express the change in ozone as a function of measurable parameters, specific to the effect being studied. For the aircraft operations assessment, these parameters include numbers and types of aircraft, cruise altitude, and projected engine technology. For the Space Shuttle operations assessment, the parameters include the latest traffic model which gives the number of projected flights as a function of time. For the chloro-

fluoromethane assessment, the input parameter is the rate of release to the atmosphere. Figure 6 gives a flow diagram for each of the assessments. For the aircraft, FAA will provide the latest traffic model and NASA's Office of Aeronautics and Space Technology (OAST) will make the projections on aircraft engine modification. The result is a NASA report to be submitted to the FAA for possible use in their regulatory function.

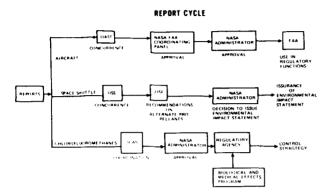


Figure 6

The overall report on Space Shuttle operations is the responsibility of NASA's Office of Space Flight (OSF). As part of this report, NASA's Life Sciences Directorate will comment on possible biological and medical effects caused by Space Shuttle operations. These comments will be incorporated into the report that will be submitted to the NASA Administrator for his use in making decisions on possible system changes in the Space Shuttle design. The CFM report will be prepared by NASA and given to the appropriate Federal agency or agencies for use in their rulemaking procedures that could lead to some form of regulatory action affecting the release of the CFMs.

The schedules for producing the reports are shown in Table 5. The procedure for each of the reports is similar. There is a period in which predictions are made using one-dimensional models and the newest data available. This is followed by workshops where the theorists and experimentalists discuss the reasons for the differences among and uncertainties in these model predictions. This meeting is followed by a draft report that undergoes extensive review. The final report is then prepared and issued to the appropriate authorities. Ames Research Center (ARC) has accepted responsibility for producing the aircraft report. The Johnson Space Center (JSC) is responsible for the Space Shuttle report and the Goddard Space Flight Center has the responsibility for producing the reports on the CFMs.

Table 5. Schedule for Preparation of Reports

Aircra	ft
Predictive Modeling	June-November 1976
Workshop at ARC	November 1976
Draft Assessment Report (ARC)	December 1976
Review of Report	January-March 1977
Final Report	April 1977
Space Sh	uttle
Predictive Modeling	July 1975-February 1976
Workshop at JSC	March 1976
Assessment Report	March 1976
Review of Report	April 1976
Recommendations to Administrate	or (OSF) May 1976
Chlorofluoro	methanes
Preliminary Report (GSFC)	September 1976
Predictive Modeling	September-December 1976
Workshop at GSFC	January 197
Draft Assessment Report	February 197
Review of Report	March-August 197
Final Report	September 197

For the report schedules to be met, results from the field measurements, laboratory experiments, and theoretical studies must be available during the required time frame. Consequently, appropriate milestones have been established for each of the assessments. Figure 7 shows the milestone schedule for Aircraft Assessment for the next five years. Annual meetings, to be held jointly with FAA, are scheduled for the month of May. Detailed experiments are not defined past CY 1977 although GASP is expected to continue into the 1980s. The program structure beyond 1977 depends in part upon the requirements of the regulatory agencies such as FAA and EPA.

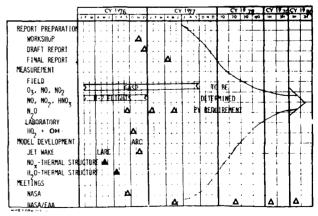


Figure 7.-Aircraft Assessment

The milestone schedule for the Space Shuttle Assessment is shown in Figure 8. Although the final report on the effects of Space Shuttle operations was scheduled for May 1976, there will be an annual reassessment in each of the next 4 years to take advantage of new laboratory and field data and improvements in modeling techniques.

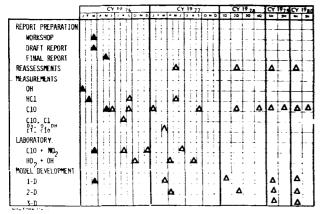


Figure 8.-Space Shuttle Assessments

At those times, decisions affecting system design and changes can also be re-examined. This time scale is reasonable, as the Space Shuttle operations are not expected to reach 60 launches per year before 1983 Also any perturbations in the stratosphere caused by Space Shuttle operations diminish rapidly when the launches stop, unlike the perturbations caused by CFMs, for which there is a long time lag between release at the surface and arrival in the stratosphere.

Figure 9 shows the corresponding schedule for the chlorofluoromethanes. The final report is due in September 1977. This is the date NASA has indicated to the Congress that the report will be submitted to the appropriate regulatory agency for use in its rulemaking procedures which could lead to some regulatory action affecting the CFMs. We expect that reassessment of the CFM effects will be made subsequent to the final report, although these dates are not shown on the charts.

As new potential threats to the stratospheric chemistry and physics are identified, they will be added to the program and a timetable for their assessment will be developed.

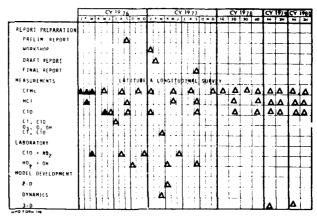


Figure 9.-Chlorofluoromethane Assessment

Figure 10 shows the projection for the overall program and indicates that these assessments are expected to be a major part of the program only for the first few years.

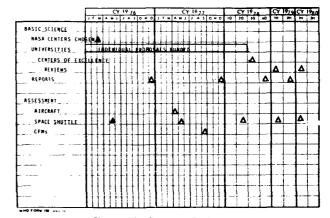


Figure 10.—Program Projections

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# V. INSTITUTIONAL BASE FOR LONG-TERM PROGRAM

NASA believes it can best accomplish its goals in long-term atmospheric research by assisting in the establishment and concentration of an institutional base for conducting atmospheric research. The base should be an appropriate combination of talent from universities and from within NASA to ensure imaginative research efforts, knowledgeable direction of the effort and the appropriate application of research results.

Active participation in the guidance of the NASA program by the university community is through the Stratospheric Research Advisory Committee (SRAC).

This committee is composed of experts in several scientific disciplines from universities and other institutions who have demonstrated competence in atmospheric science. The committee, which held its first meeting on July 31 and August 1, 1975, is advising NASA on the application of its resources to the most important aspects of stratospheric research, ensuring that NASA is conducting an integrated stratospheric research program, ensuring that NASA's efforts complement the work of other Federal agencies in stratospheric research, and advising NASA specifically on current and urgent problems as they relate to the upper atmosphere. Upon request, the committee will offer its services to other Federal agencies in areas such as the CFMs, where there is a common interest between NASA's program and other Federal programs. Through SRAC, a measurement strategy is being developed that will allow decisions to be made in the field measurement program as to the type of measurements, the frequency, and the selection of platforms. SRAC is expected to play an active role in the program's implementation.

Other ad hoc advisory groups will be organized to handle specific problems, such as priorities in field measurements, as they become identified. Unlike SRAC, these groups are expected to have very limited lifetimes, from a few days to a few months.

The NASA centers have traditionally served as institutional bases for NASA programs. There is a collection of outstanding talent at the centers which can be called upon to provide the necessary in-house capability for implementing the Upper Atmospheric Research Program. Two NASA installations, the Goddard Space Flight Center (GSFC) and the Jet Propulsion Laboratory (JPL) have been given major roles

in the Upper Atmospheric Research Program. GSFC is to concentrate on field measurements and theoretical studies, and JPL is to emphasize field measurements and laboratory experiments. These organizations are being asked to enhance communication among scientists, universities, industry and government organizations in atmospheric science. They are expected to solicit participation of scientists from all pertinent disciplines in understanding atmospheric phenomena. GSFC and JPL will provide the use of NASA facilities and space capabilities in the discovery and application of scientific knowledge. They will assist the academic community in utilizing opportunities for research with NASA and on NASA's space flights. A close working relationship should develop with GSFC, JPL, the universities, industry and government personnel in atmospheric research and in the application of research results. It is intended that the programs at GSFC and JPL will involve visiting scientists, organizing symposia and encouraging multi-disciplinary studies. They participate in the review of proposals, and arrange for special studies, meetings, seminars, colloquia, and summer studies.

The Ames Research Center (ARC) has a more limited role as an institutional base. ARC is to concentrate on field measurements utilizing aircraft with a low-level modeling effort to support the aircraft studies. They are expected to fully support GSFC and JPL in the field measurements as they relate to the aircraft as a measuring platform. The Langley Research Center (LaRC) and the Lewis Research Center (LeRC) both give limited support to the Upper Atmospheric Research Program. The GASP is at LeRC and serves to define LeRC's limited role in the program. LaRC is the primary center for the Office of Application (OA) related activities in stratospheric research. It is through this role that LaRC is expected to contribute to the OSS-based Upper Atmospheric Research Program.

Active participation by the academic community is through the normal NASA practice of encouraging the submission of research proposals to the program office. NASA plans to issue a "Dear Colleague" letter inviting scientists to submit unsolicited proposals in those areas of science described in the long-term program. This letter is expected to be issued during the summer of

1976 with funds becoming available October 1, 1976. There is already active university and college participation in the program through the funding of unsolicited proposals already received. These are identified in the Appendix.

It is NASA's long-range plan to support academic research by encouraging universities and colleges to submit quality proposals for funding. If, after 2 or 3 years, there is a concentration of outstanding researchers at particular universities or colleges that have submitted

successful proposals to the program, NASA will consider providing to these institutions a base level of block funding for their atmospheric sciences activities. At this time these institutions could indeed be called "centers of excellence" in atmospheric science. However, it is expected that even after the "centers of excellence" are identified, individual proposals from other institutions will be considered for funding when the work being proposed is consistent with the long-range objectives of the Upper Atmospheric Research Program.

# VI. RESOURCES PLAN

The NASA effort in stratospheric research in FY 1975 was approximately \$7 million, shared by four NASA offices: Office of Space Flight (OSF, \$1.085 million), Office of Applications (OA, \$2.977 million), Office of Aeronautics and Space Technology (OAST, \$1.842 million) and Office of Space Science (OSS, \$1.133 million).

Before NASA's expanded role in upper atmospheric research, \$7 million was included in the FY 1976 budget request for stratospheric research and was proposed for continuance of work at universities and the NASA centers.

The assignment of overall responsibility for NASA's stratospheric research activities to the OSS required the transfer of FY 76 funds from other NASA program offices to OSS.

Approximately \$2.8 million were transferred to OSS from OSF and OAST. In addition, NASA reprogrammed \$3.5 million for upper atmospheric research which, with the \$1.1 million already in OSS, made the total FY 76 funding approximately \$7.4 million. For the transition period the total is approximately \$2.2 million with \$450,000 being transferred from OSF and \$699,000 from OAST. In FY 77, the budget for the Upper Atmospheric Research Program, exclusive of the satellite

systems work in NASA's Office of Applications, is recommended at \$11.6 million. This amount is expected to represent a level-of-effort for the next 4 years.

Table 6 shows the projected budget for Upper Atmospheric Research through FY 1980. For future years, the funds for the major categories, basic science and assessment, have been assigned somewhat arbitrarily. The program will not be constrained to maintain this division. For example, if the question of the CFM's effect in the stratosphere has been resolved by CY 1978, funds earmarked for CFM assessment could be placed in the basic science program. Conversely, if a new chemical is identified as being a potential threat to stratospheric ozone, the necessary funding could be taken from the basic science program and a viable program can still be maintained.

The detailed breakdown under basic science for field, laboratory and theoretical studies reflects the program's goal for providing, during the next few years, 60 percent of its resources to field measurements, 20 percent to laboratory experiments, and 20 percent to theoretical studies.

The overall budget is expected to remain constant at approximately \$11.6 million. However, the details are subject to change.

Table 6. Upper Atmospheric Research Office Funding (in millions of dollars)

		Transition				
	FY <b>76</b>	Period	FY 77	FY 78	FY 79	FY 80
Basic Science	2.0	0.5	2.6	6.7	8.2	9.2
Field Measurements	1.2	0.3	1.6	4.0	4.9	4.9
Laboratory Experiments	0.4	0.1	0.5	1.4	1.7	1.9
Theoretical Studies	0.4	0.1	0.5	1.3	1.6	1.8
Assessment	5.4	1.7	9.0	4.9	3.4	2.4
Aircraft	2.9	0.7	3.3	1.3	1.3	1.3
Space Shuttle	1.0	0.5	0.2	0.1	0.1	0.1
CFMs	1.5	0.5	5.5	3.5	2.0	1.0
TOTALS	7.4	2.2	11.6	11.6	11.6	11.6

# VII. ATMOSPHERIC RESEARCH PROGRAMS IN OTHER FEDERAL AGENCIES

Several other agencies of the Federal Government have established programs designed to contribute to a better understanding of the upper atmosphere.

Since 1974, the Interdepartmental Committee for Atmospheric Sciences (ICAS), established by the Federal Council for Science and Technology, has acted as coordinator for Federal agencies involved in atmospheric science as it relates to the ozone problem. ICAS is composed of members from DOD, DOT, DOC, ERDA, DOA, DOI, DOS, EPA, NSF, and NASA.

To help NASA in performing its lead agency role in instrumentation and measuring systems, a subcommittee of ICAS was established to hasten the development of new instruments and measuring systems which would be many times more sensitive than existing techniques. This Subcommittee on Instrumentation and Measuring Systems (SIMS) is chaired by a NASA representative and has held a series of meetings. The Federal agencies represented on the SIMS and their agency interests are given in Table 7.

# Table 7. Subcommittee on Instrumentation and Measuring Systems (SIMS)

# Members

Dr. James King, Jr., Chairman

Capt. Hugh Albers, ICAS

Dr. Frank Niles, USABRL

Ms. Joan Barriage, FAA

Dr. Herbert Wiser, EPA

Dr. Arthur L. Schmeltekopf, NOAA

Dr. Gene W. Adams, NSF

Mr. Thomas Gross, ERDA

Dr. Rocco Narcisi, AFGL

Dr. Darrell Strobel, NRL

Many of the Federal agencies have, like NASA, structured their programs around the stratospheric ozone problem and use field measurements, laboratory experiments and theoretical studies for program implementation.

#### DEPARTMENT OF AGRICULTURE

The Agricultural Research Service studies climate factors, including ozone depletion, and how climatic changes affect insects, plants, and disease. Broad- and narrow-band UV radiation studies are conducted to simulate the conditions caused by ozone depletion in the stratosphere.

#### THE DEPARTMENT OF COMMERCE

#### Field Measurements

# Air Resources Lab of NOAA

This laboratory operates GMCC (Geophysical Monitoring for Climatic Change) Stations at four locations around the world. The stations are at Point Barrow (Alaska), Mauna Loa (Hawaii), South Pole, and the new station at American Samoa. Several other stations are in operation in the U.S. for certain measurements. At these sites the concentration of the following gases are measured: CO<sub>2</sub>, O<sub>3</sub> (total column), surface O<sub>3</sub>, CFCl<sub>3</sub>, CCl<sub>4</sub>, and at some stations NO<sub>x</sub>, NH<sub>3</sub>, H<sub>2</sub>S, SO<sub>2</sub>. Aerosol particles are measured by several methods at all stations. Measurements of solar radiation at several wavelengths including erythemal wavelengths are made at several stations. Finally the composition of precipitation is determined at several stations.

## Aeronomy Laboratories of NOAA

A new method for measuring stratospheric, tropospheric, and total column NO<sub>2</sub> has recently been developed. This instrument is now operating from Fritz Peak Observatory, near Rollinsville, Colorado and from Point Barrow, Alaska. The very large seasonal and latitudinal variation of the NO<sub>2</sub> density is being studied from these stations.

OH total column has been measured from the Fritz Peak Observatory using the OH absorption at 308.3 nm. The instrument required is a very high-resolution interferometer. This apparatus is being improved and the measurements should continue in 1977. A system to

measure the surface NO is being developed and will be installed at some of the GMCC stations. This system uses chemiluminescence detection. However, because of the possible interference from other species at the surface and because of the low surface concentrations of NO, some additional research is necessary before the instrument is ready for routine use.

The NO<sub>2</sub> atmospheric absorption measurements have also been conducted from aircraft. These flights are flown so that twilight is maintained over the whole flight and so that a profile as a function of latitude can be obtained. The results from these flights have shown a striking latitudinal dependence of NO<sub>2</sub> concentrations.

Whole air samples have been taken from aircraft. It was found that surface samples showed wide variability, and thus baseline values for various gases were hard to determine from surface samples. Aircraft samples showed less variability and thus better tropospheric base line numbers can be obtained. CFCl<sub>3</sub>, CF<sub>2</sub>Cl<sub>2</sub>, CCl<sub>4</sub>, N<sub>2</sub>O and several other gases have been measured from these samples. Other trace gases are known to be present, but calibration and sample stability tests have not yet been done on these gases.

Eight whole air samples have been obtained from former air flights. The sampling valve was found to have some problems so that a new sampling system was designed. This system has now been tested and the new whole air sampling packages were ready in December 1975. After that time, a series of flights was started to obtain both seasonal and latitudinal effects on the trace constituent concentrations in the upper troposphere and stratosphere. Several problems involving the long-term stability of the samples in the sample containers must still be understood before measurements can be made on CCl<sub>4</sub> or CH<sub>3</sub>Cl, for example. At present only CFCl<sub>3</sub>, CF<sub>2</sub>Cl<sub>2</sub> and N<sub>2</sub>O can be measured with confidence.

A resonance fluorescence system for measuring ClO is being developed. It is hoped that measurements can be made by the end of 1976.

#### Laboratory Experiments

Aeronomy Laboratory of NOAA.

An apparatus has been constructed to measure directly the destruction of  $O(^1D)$  by various atmospheric species as a function of temperature. Ozone is photolyzed by laser light at 266 nm and the  $O(^1D)$  is observed by its red line emission. The time rate of decay of this light is measured as a function of the concentration of various reactants. To date the absolute rate constants for the reactions with various atmospheric

gases have been obtained as well as the temperature dependence of some of them. The absolute rate of reaction was generally found to be a factor of two different from that accepted in the literature and the size and direction of the temperature dependence was unexpected. These results thus modify the theory of the odd-nitrogen cycle in the atmosphere.

Measurements of the reaction rate constants for the ions expected to be present in the troposphere in reasonable abundances have been made with CFCl<sub>3</sub> and CF<sub>2</sub>Cl<sub>2</sub> and have been found not to be significant. Calculations and measurements have also been made regarding the removal of Cl, ClO, or HCl from the stratosphere by ion-molecule reactions. The conclusions of these measurements and calculations show that ion-molecule reactions are extremely unlikely to have any influence on the fluorocarbon chemistry in the earth's atmosphere. This study is conducted jointly by NBS and NOAA.

Measurements of the reactivity of OH with various chlorofluorocarbons have been made. This system uses laser magnetic resonance as a detector for OH and uses a flow mixing system for measuring the reaction rates. Reactions with CFCl<sub>3</sub> and CF<sub>2</sub>Cl<sub>2</sub> are immeasureably slow, but the reactivity is larger for species containing H or carbon double bonds. As environmentally acceptable substitutions for F-11 and F-12 must be removed in the troposphere and reaction with OH is the most likely tropospheric removal process, these measurements will help find reasonable substitutes for F-11 and F-12.

#### National Bureau of Standards

There is an ongoing program in photolysis to determine the chlorine quantum yields and absorption cross sections of various halocarbons. Quantum yields will be determined for HCF<sub>2</sub>Cl, HCFCl<sub>2</sub>, H<sub>2</sub>CFCl, and CCl<sub>4</sub>. Absorption cross section measurements (180 to 230 nm) will be made for these compounds and also for CFCl<sub>3</sub>, CF<sub>2</sub>Cl<sub>2</sub>, and CH<sub>3</sub>Cl.

The rate constant for  $Cl + O_3 \rightarrow ClO + O_2$  was recently measured at stratospheric temperatures by a flash photolysis-resonance fluorescence experiment. Rates of the following reactions will be determined, including temperature dependencies:  $O + ClO \rightarrow Cl + O_2$  and  $NO + ClO \rightarrow Cl + NO_2$ .

# Theoretical Calculations

#### Aeronomy Laboratory of NOAA

One- and two-dimensional model calculations are made, including all of the known chemistry, to predict

the effects on the ozone layer by various trace constituents, with special emphasis on the effects of the fluorocarbons. These models use empirical values for the circulation and diffusion parameters, but include the photolytic and chemical kinetics effects.

# Geophysical Fluid Dynamics Laboratory of NOAA

Three-dimensional general circulation model calculations are made without the inclusion of chemistry. These calculations are used to test the validity of the assumptions made in the one- and two-dimensional models.

#### DEPARTMENT OF DEFENSE

#### Air Force

The Air Force Geophysics Laboratory (AFGL) stratospheric program exists to answer environmental impact questions regarding USAF aircraft and missile operations. The program indirectly contributes to the U.S. plan to determine possible impact of halocarbons on ozone. The AFGL program consists of field measurements, laboratory studies directed toward heterogeneous reactions, and ultraviolet cross sections and limited numerical simulation of the stratosphere. The field measurements are described below.

#### **Balloon Measurements**

A cryogenic collector, flown on a balloon, is used to collect 22.4 liters STP (1 g mole) samples of stratospheric air for subsequent laboratory analysis for stratospheric constituents. A calibrated ultraviolet spectrometer with  $\sim 0.1$  Å resolution is flown to measure the absolute solar flux in the wavelength range of 2000 to 3000 Å as a function of altitude. This is measured to determine photon input and ozone concentration in the stratosphere. Stratospheric turbulence and eddy diffusion are measured in situ with a new sensor flown on a balloon and by photographic observation of smoke trails.

#### Army

The Army does not have an identifiable stratospheric research program. Stratospheric research is part of more encompassing programs that have as their objectives to determine, understand, and predict the atmospheric environment likely to be encountered by communications systems or during the conduct of ballistic missile defense; to assess the change in the atmospheric environment induced by nuclear or non-nuclear events; to identify mitigative or circumventive techniques for

lessening the degrading effects of the atmospheric environment; and to interrelate the meteorological, physical, and chemical aspects of the atmosphere simultaneously. The approach being utilized to reach these objectives is to identify important atmospheric recovery processes including reactions and reaction rates, to measure the concentrations of atmospheric constituents under prescribed conditions, to conduct laboratory experiments for measuring reaction rate coefficients and physical properties of atmospheric constituents, to investigate atmospheric phenomena that yield information on atmospheric effects produced by nuclear bursts, and to develop theoretical models of the atmosphere for specified conditions.

#### Field Measurements

Atmospheric measurements are made utilizing ground-based, balloon-borne, and rocket probes.

Rocket and Ground-Based Measurements. The Atmospheric Sciences Laboratory (ASL) operates three. ideally-located, rocket-sounding stations as part of the Meteorological Rocket Network. In the equatorial zone is the station at Fort Sherman, Canal Zone; in the temperate zone is the station at White Sands Missile Range (WSMR), New Mexico; in the arctic zone is the station at Poker Flat, Alaska. The basic schedule calls for three soundings per week (Monday, Wednesday, and Friday) at each station. Each sounding includes a rawinsonde and rocketsonde and provides measurements and calculations of atmospheric temperature, pressure, density, and winds from the surface to an altitude of 70 km. Scheduled to be added is an ozonesonde. A Dobson spectrophotometer is used daily, Monday through Friday, to measure total column ozone at WSMR. Blunt probes and Gerdien condenser probes suspended from parachutes carried aloft by rockets are being utilized to study ions in the stratosphere.

Balloon-Borne Measurements. High-altitude, zero-pressure balloons have been used to carry aloft a number of scientific payloads. ASL was one of the sponsors of STRATCOM V (fifth in a series of balloon flights by ASL to investigate stratospheric composition) which was successfully flown on September 24, 1975. STRATCOM V was a multi-instrument, balloon-based, correlated study of stratospheric composition, dynamics, and thermodynamics in the altitude of 20 to 38 km.

Emission and absorption spectroscopy in the infrared is being used to determine the concentrations of several atmospheric species up to the float altitude of the balloon. Three flights with an emission spectrometer were made over Alaska during April/May 75. Another

series of flights took place over Alaska in April/May 1976.

Investigations of ions in the stratosphere are being carried out with blunt probes and Gerdien condenser probes. Also efforts are being made to develop a mass spectrometer to identify and measure both positively and negatively charged species. Ion mass spectrometry could be a very sensitive method for the measurement for certain minor constituents.

# Navy

The Navy has historically conducted a broad program of basic research on the atmosphere and the ocean-atmosphere interface. Significant attention is devoted to the stratosphere to determine possible adverse effects of Navy aircraft and missile systems on that vital stratum and to assess the possibilities of events adversely affecting naval communications and detection and control systems.

The Navy research program consists, in part, of ground-based, ship, aircraft, and balloon-borne sampling of the atmosphere to determine concentrations of ozone, water vapor, fluorocarbons, carbon tetrachloride, carbon monoxide, and particulates. Some of these constituents serve as chemical tracers of air motion.

# DEPARTMENT OF TRANSPORTATION

#### FAA

The Federal Aviation Administration's Office of Environmental Quality has established the High Altitude Pollution Program (HAPP). The objective of HAPP is to quantitatively determine the requirements for reduced cruise-altitude exhaust emissions and, in conjunction with the Environmental Protection Agency (EPA) and the International Civil Aviation Organization (ICAO), to ensure that, if necessary, appropriate regulatory action is taken to avoid environmental degradation. HAPP is being organized along the lines of field measurements, laboratory measurements and modeling. The field measurements include: (1) instrument development, (2) alternate measurement platforms, (3) WB-57F aircraft support, (4) tracers of atmospheric motions, (5) analysis and interpretation of existing data as they relate to aircraft emissions, and (6) measurements of trace species. The laboratory measurements include (1) gas-phase reaction kinetics, (2) photolytic quantum yields, (3) chemical data evaluation, (4) heteorogeneous equilibria and kinetics, (5) molecular spectroscopy, and (6) novel measurement techniques. The modeling effort includes transport-kinetics, photochemical kinetics, and radiative transfer.

A program plan for HAPP is being developed and will contain detailed descriptions of all of these topics.

# ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION

#### Field Measurements

# Project Airstream

A WB-57F aircraft flies particulates, whole air, and tritium samplers three times a year at four altitudes ranging from 40,000 to 63,000 ft to provide a nearly continuous sampling profile from 75°N to 10°S latitude along the west coast of the Western Hemisphere. Filters and the whole air samplers are sent to the ERDA Health and Safety Laboratory for analysis of particulates and gaseous radioactivity and other constituents including F-11 and sulfur hexafluoride (SF<sub>6</sub>).

# Project Ash Can

High-altitude balloons carry particulate and gaseous samplers to altitudes of 70, 80, and 90,000 ft three times a year from New Mexico and annually from Alaska and Panama. Filters are provided to the National Center for Atmospheric Research under a cooperative agreement for the measurement of several trace constituents including hydrogen chloride (HCl). A York University nitric oxide (NO) sensor and an ozone (O<sub>3</sub>) sensor are included on most flights from New Mexico. A development effort is being supported to provide near simultaneous measurements of nitrogen dioxide (NO<sub>2</sub>).

# Stratcom

ERDA provides partial support for an interagency, multi-instrumented, balloon-borne study of stratospheric composition, dynamics, and thermodynamics. Two successful flights in October 1975 carried some 40 instruments to make more than 20 different types of atmospheric measurements up to 38 km including solar spectrum and ozone density with a UV spectrometer. Additional flights in this series may be flown.

# **Laboratory Experiments**

# University of California, Irvine

The stratospheric photochemical sink for F-12 and F-11 will continue to be investigated, with emphasis on the consequences of the chemical reactions of Cl atoms

with ozone. Laboratory determinations will be made of the concentrations of F-12 and F-11 in gas samples collected in the stratosphere by balloon and/or rocket.

# **ENVIRONMENTAL PROTECTION AGENCY**

The EPA Program consists principally of Field Measurements and Laboratory Experiments concentrating on the behavior of the fluorocarbons in the lower atmosphere.

#### **Field Measurements**

# Tropospheric Halocarbons

The task is designed to measure the distribution of halogenated compounds in rural and urban areas, and over water. The measuring technique is gas chromatography – mass spectroscopy, which is also used to identify new types of halocarbons. The Principal Investigator (PI) is Rasmussen of Washington State University.

Another task is also designed to study the tropospheric distribution and chemical behavior of halocarbons through atmospheric analyses at urban, rural and maritime locations. The PI is Singh of Stanford Research Institute.

A third task to analyze the halocarbons in the troposphere uses a collection technique where samples collected at urban, rural and maritime locations are analyzed in the laboratory using infrared spectroscopic techniques. The infrared technique can measure trace gases with mixing ratios as low as one in 10<sup>12</sup>. The Pl is Hanst of EPA.

# Tropospheric Hydrogen Chloride

Line-reversal infrared correlation spectroscopy is used to assess the removal rates of HCl measured in urban and rural regions. The objective is to identify HCl sources and sinks in the troposphere. The contractor is Northrop Corporation.

# **Laboratory Experiments**

# Tropospheric Photochemistry of Halocarbons

Laboratory experiments are used to determine the rates of photooxidation of halogenated compounds under simulated tropospheric conditions. A long-path photochemical reactor is used for the simulation studies and a Fourier transform spectrometer is used to monitor the progress of chemical transformations. The PI is Shaw at Ohio State University.

# Stratospheric Chemistry of Halocarbons

Stratospheric conditions are simulated in a photochemical reactor where O<sub>3</sub>, ClO, Cl, O, and other pertinent species are created and their interactions are measured. Also, there is direct photolysis of halogenated methanes, phosgene and carbonyl fluoride in the photochemical reactor. The contractor is the Northrop Corporation.

# Halocarbon Reaction in the Atmosphere

Laboratory experiments are used to determine the rates of degradation of halocarbon pollutants in the troposphere and stratosphere. Studies are made of the lifetime and eventual fate of the intermediate products of the photooxidation. The PI is Soloman at IITRI.

# Chemistry of Degradation

Laboratory experiments are used to determine the chemical mechanisms of degradation of halogenated pollutants. Photooxidation is carried out under simulated atmospheric conditions in a reaction chamber that permits observation of the consumption of reactants and the formation of products. The PI is Hanst of EPA.

#### THE NATIONAL SCIENCE FOUNDATION

The National Science Foundation (NSF) awards grants to university researchers and others for investigations into the basic physics and chemistry of the Earth's atmosphere. The chemistry program supports the application of millimeter wave spectroscopic techniques (developed for interplanetary and galactic studies) to the measurement of altitude profiles of minor species in the Earth's atmosphere, and the use of high-resolution spectrometers for studies of the total column content of OH. The meteorology program supports a broad spectrum of research into the dynamic, physical, and chemical processes in the lower atmosphere and stratosphere. The aeronomy program supports laboratory studies of chemical processes of stratospheric interest and also supports the development of techniques for measuring stratospheric constituents.

NSF also manages the National Center for Atmospheric Research (NCAR), which has an upper atmospheric project consisting of satellite-borne experiments as well as in-situ measurements to determine the chemical composition of the upper atmosphere. Stratospheric balloon measurements of various trace gases including the chlorofluoromethanes and

tropospheric measurements of gases and aerosols are also part of the upper atmospheric project. The modeling

efforts include the development of both tropospheric and stratospheric models.

#### VIII. RELATIONS WITH INDUSTRY

The present short-term problem of the impact on the environment from releases of CFMs has resulted in a disagreement between the industrial manufacturers of fluorocarbons and the environmentalists. The industrial concerns and efforts are being coordinated by the Manufacturing Chemists Association (MCA), which at present is conducting a program of assessment similar to NASA's program. The environmentalists are usually heard through congressional hearings and public media. MCA is currently funding research at a level of about \$1.1 million in Canada and the United States, with plans for about \$5 million during a 3-year period to develop enough scientific evidence to define the impact of fluorocarbons on the stratosphere.

NASA and MCA are openly discussing each other's efforts with the goal of utilizing each organization's resources and unique capabilities to efficiently assess the

fluorocarbon threat. Periodic meetings are held between MCA and NASA representatives to discuss the progress in the respective programs and to check for unnecessary duplication in the two programs. Some investigators work in both programs. Each organization is aware of these cases and gives them special attention during the discussions.

The MCA funded tasks are listed in the Appendix along with those from NASA and the other Federal agencies.

Other NASA relations with industry concern proposals from industrial scientists and the funding of those proposals once they have been reviewed and accepted. The "Dear Colleague" letter mentioned previously will also be sent to industrial organizations encouraging them to participate in the NASA program.

#### IX. THE INTERNATIONAL DIMENSION

Stratospheric pollution is a problem affecting the entire globe, not just localized areas near the regions where the pollutants are released. Further, CFMs are produced by various nations, the United States accounting for about one-half of the total. If laws are enacted in the United States to limit the releases, the problem cannot be solved without corresponding actions on the part of other nations. Congress has expressed concern to NASA that international participation in upper atmospheric research must be encouraged so that lawmakers in other countries will have access to the scientific expertise necessary to evaluate and to respond to the US actions. For example, the decision issued by the Secretary of Transportation, William T. Coleman, Jr., on February 4, 1976, on the Concorde supersonic transport requested that an agreement be negotiated with France and Great Britain for a monitoring system for measuring atmospheric ozone. NASA is participating in an interagency agreement to provide support to the U.S. Government's obligation under the tripartite agreement.

#### **Initiatives to Develop International Cooperation**

Consistent with congressional legislation to encourage international cooperation, NASA has undertaken initiatives with a number of foreign agencies to stimulate international coordination of stratospheric research in general and, in particular, to identify opportunities for specific cooperative projects which would contribute significantly to the NASA program. These cooperative projects are undertaken with foreign government organizations on a no-exchange-of-funds basis under arrangements providing that each side bear the cost of carrying out its own responsibilities in the project.

In addition to raising the level of awareness of the CFM problem, NASA initiatives have yielded concrete prospects for expanded cooperative stratospheric research.

NASA representatives visited the United Kingdom, France, and Belgium in summer 1975 to determine what these countries were doing in stratospheric research in order to identify opportunities for cooperative and complementary activities.

There is a substantial amount of upper atmospheric research already being conducted in the United Kingdom, France, and Belgium.

The Centre Nationale d'Études Spatiales (CNES), the French National Space Agency, maintains a strong balloon-based observation program with launches from both hemispheres. They started in 1960 and presently launch about 80 balloons per year. Launches are made to support their own research programs as well as those of other countries. Two remote-sensing spectroradiometers and several Lidar systems have been developed in France and flown on balloons. It is expected that they will be proposed for Spacelab flight in the early 1980's in collaboration with American and Belgian teams.

French, British, and Belgian scientists have had important experiences in satellite programs directed toward upper atmospheric research. Oxford University, supported by the Science Research Council (SRC) of the United Kingdom, maintains an interest in the dynamics of the upper atmosphere and has developed radiometers flown successfully on the Nimbus 4, 5 and 6 satellites to obtain data on motions, temperatures, and a variety of other parameters. With sponsorship from the SRC, Oxford is currently developing a Stratospheric and Mesospheric Sounder (SAMS) to measure  $H_2O$ ,  $N_2O$ ,  $CH_4$ , CO, and NO on Nimbus-G, scheduled for launch in 1978. They also have a modest modeling effort to support this program.

The programs in Europe emphasize platform development and field measurements. The US programs are able to devote more effort to atmospheric modeling because of the availability of large computers necessary for large scale modeling.

Programs in France and Belgium have not been strongly oriented to the CFM issue. However, there is growing awareness of the problem and definite interest has been shown in cooperating with NASA in upper atmospheric research.

In order to increase exchange of scientific information and views in this area, NASA invited three outstanding European scientists to participate on NASA's Stratospheric Research Advisory Committee.

In France, promising possibilities for cooperative projects were discussed with CNES and were defined in more detail during the CNES/NASA program reviews held in Washington, DC in September 1975. Work is progressing on a possible joint program of simultaneous measurements of trace constituents using US and French instruments flown together on NASA aircraft

and on European balloon platforms. A prospective cooperative transatlantic stratospheric balloon project is being explored. The feasibility of accommodating the NASA Global Air Sampling Program (GASP) instrumentation on the Concorde to acquire atmospheric data at stratospheric altitudes to contribute to the long-term data base is also being investigated with authorities from France and the United Kingdom.

NASA is also exploring possibilities for cooperation with government science organizations in other countries. The topic has been raised during cooperative program review discussions in the Federal Republic of Germany, the Netherlands and Denmark. Letters soliciting proposals for joint stratospheric research work have been sent to appropriate government organizations in Australia and Japan. In response to a NASA initiative, the Canadian Interdepartmental Committee on Space has designated a prime point of contact in Canada to work with NASA in developing cooperative projects in stratospheric research with Canadian government agencies.

Responding to a suggestion by NASA, the Italian Aerospace Research Center has amplified a cooperative satellite proposal to NASA by adding a radiometer capability to detect atmospheric ozone to one of the two proposed San Marco D spacecraft. Formal arrangements for the project are now being concluded.

NASA is currently working with the University of Stockholm and the Swedish Board of Space Activities to define a prospective collaborative project in observation of aerosol layers or noctilucent cloud studies using NASA laser equipment on loan to the University of Stockholm.

Japan has indicated an interest in cooperating with NASA on the international problem through the Japan Meteorological Agency and the Institute of Space and Aeronautical Sciences at the University of Tokyo.

With regard to potential cooperation with the Soviet Academy of Sciences, the possibility of undertaking joint or coordinated investigations on problems affecting the Earth's atmosphere and oceans on a global scale has been raised as one of the major thrusts of future NASA/USSR Academy cooperative activity. The ozone question has been identified as a prime candidate for study.

#### **International Meetings**

There is a continuing need to have international meetings in which the scientists participate, hear about work by other researchers, and have an opportunity to exchange views. One such gathering was held in Grenoble, France, at the meeting of the XVI General

Assembly of the International Union of Geodesy and Geophysics on August 25 to September 6, 1975. During this meeting, there was a special half-day session devoted exclusively to fluorocarbons in the stratosphere. The exposure of the fluorocarbon issue at such meetings contributes to a more thorough appreciation of the nature of the problem as well as to a review of information concerning ongoing research work.

Extensive foreign participation in and attendance at the NASA-sponsored International Conference on the Stratosphere and Related Problems at Logan, Utah, in September 1976 is anticipated.

#### Relations with International Agencies

The Committee on Atmospheric Sciences (CAS) of the World Meteorological Organization (WMO) has drafted details of a WMO Proposal for a Global Ozone Research and Monitoring Project to determine the impact of man on the stratospheric ozone budget. The adoption of this program was considered by the Geneva meeting of WMO held in May 1976. Each nation's representative is expected to work with the agencies within his own country to secure the cooperation needed to undertake the pertinent portions of the Program. NASA will be coordinating its Upper Atmospheric Research Program with the WMO Program via the U.S. Representative to WMO, Dr. Robert White, the Administrator of NOAA.

A second international organization, the Inter-Union Special Committee on Solar Terrestrial Physics (SCOSTEP), with the cooperation of the Committee on Space Research (COSPAR), the International Union of Radio Science (URSI), the International Association of Geomagnetism and Aeronomy (IAGA), and the International Association for Meteorology and Atmospheric Physics (IAMAP), is organizing a "Middle Atmosphere Program" (MAP). The major aim of MAP is the development of an adequate description and understanding of the atmosphere in the altitude range of 15 to 100 km, which includes the stratosphere and mesosphere, particularly in relation to the global fields of (1) density, pressure and temperature, (2) composition, (3) motion (on all scales) and (4) the interaction between these fields. The program will require intensive observations, so that interactions may be determined, and extensive observations so that the global picture is complete. A planning conference was held June 21-24, 1976 at Urbana, Illinois. NASA contributed financially to services required to conduct this conference and representatives from NASA were in attendance.

NASA coordinates its activities with other international programs through its memberships on the Subcommittee on Stratospheric Pollution, Committee on International Environmental Affairs, sponsored by the Department of State. This committee works with such international organizations as: Organisation for Economic Co-operation and Development (OECD), United

Nations Environment Programme (UNEP), NATO Committee on Challenges to Modern Society (NATO/CCMS), and Economic Commission for Europe (ECE).

#### APPENDIX

#### NASA Funded Research Projects

Investigator	University /Institution	Project Description
L. Acton	Lockheed Research Laboratory	Heliometer mapping of solar x-rays
A. Aikin	NASA/Goddard Space Flight Center	Photoionization mass spectroscopy
J. Anderson	University of Michigan	Stratospheric measurements using resonance fluorescence techniques
J. Arveson	NASA/Ames Research Center	Halocarbon measurements at U-2 aircraft altitudes
H. Ashkenas	Jet Propulsion Laboratory	Turbulent diffusion in the stratosphere and troposphere
K. Baker	Utah State University	Stratospheric processes using superpressure balloons
D. Barkstrom	George Washington University	Radiative transfer models
C. Barth	University of Colorado	Night-time rocket profiles of stratospheric species
A. Belmont	Control Data Corporation	Analysis of GASP ozone trends and latitudinal variations
R. Boese	NASA/Ames Research Center	Laboratory spectra of stratospheric species
D. Buhl	NASA/Goddard Space Flight Center	Measurement of stratospheric molecules with a millimeter wave radiometer
J. Chamberlain	Rice University	Radiative theory
W. Chu	Old Dominion University	SAGE & SAMII data reduction
E. Chupp	University of New Hampshire	Gamma ray observations
R. Cicerone	University of Michigan	Theoretical investigations of stratospheric processes
R. Cicerone	University of Michigan	HALOE data interpretation
E. Cohen	Jet Propulsion Laboratory	MLS laboratory spectra
D. Cooper	NASA/Ames Research Center	Spectra of CIO
B. Conrath	NASA/Goddard Space Flight Center	Interferometer-spectrometer measurements of stratospheric species

Investigator	University/Institution	Project Description
P. Crutzen	National Center for Atmospheric Research	Theoretical models
D. Davis	University of Maryland	In situ OH measurements
D. Davis	University of Maryland	Chemical reaction rates at stratospheric conditions
K. Davis	Battelle Memorial Institute	Ground-based millimeter wave absorption measurements of CIO
A. Deepak	Old Dominion University	SAGE data analysis
W. DeMore	Jet Propulsion Laboratory	Laboratory calibration systems
W. DeMore	Jet Propulsion Laboratory	Destruction of ozone from aircraft exhaust constituents
W. DeMore	Jet Propulsion Laboratory	Photochemistry of Al <sub>2</sub> O <sub>3</sub> and HCl
T. Donahue	University of Michigan	Calculations of modifications to the thermal structure of the stratosphere
T. Donahue	University of Michigan	Airglow in the thermosphere
R. Drayson	University of Michigan	Nimbus G LIMS data analysis
I. Eberstein	NASA/Goddard Space Flight Center	Numerical models—BUV
P. Falconer	NOAA/Air Resources Laboratory	Statistical analysis of GASP data
N. Farlow	NASA/Ames Research Center	In situ aerosol sensor development
C. Farmer	Jet Propulsion Laboratory	High-speed interferometer shuttle applications
C. Farmer	Jet Propulsion Laboratory	High resolution interferometer for stratospheric measurements
G. Ferry	NASA/Ames Research Center	Aerosol measurements and analysis
W. Fite	University of Pittsburgh	lonic reactions
D. Garvin	National Bureau of Standards	Compilation of chemical kinetic and photochemical data
J. Gille	National Center for Atmospheric Research	Nimbus G LIMS data analysis

Project Description	SAGE data analysis	Aerosoi sensor development and analysis	Theoretical calculations of properties of atmosphere	Support for Climatic Impact Committee	Mesospheric ionization in winter	Development of general circulation models	Ozone data analysis	BUV experiments, rocket program	SAGE data analysis	In situ H <sub>2</sub> O sensor	Modeling of alumina aerosols	Radiative transfer and aerosols, ozone studies	Nimbus G LIMS data analysis	Assessment of ozone perturbations	International conference on the stratosphere	UV spectrum	Determination of rate parameters for stratospheric gases	Modeling of aerosols	Filter sampling of stratospheric species
University /Institution	National Center for Atmospheric Research	Oceanor I aboratories	University of Florida	National Academy of Sciences	Pennsylvania State University	NASA/Goddard Institute for Space Studies	University of Michigan	NASA/Goddard Space Flight Center	University of Arizona	NASA/Goddard Space Flight Center	University of Wyoming	Wallops Flight Center	Drexel University	NASA/Goddard Space Flight Center	Jet Propulsion Laboratory	University of Hawaii	University of Pittsburgh	State University of New York	National Center for Atmospheric Research
Investigator	G. Graves		C. Grav	A. Green	B. Gregory	L. Hale J. Hansen	D Haos	D. Heath		E. Hilsenrath	die Efection C	C. Tolling		E. Hudson	W. Lintess	W. Hoffries	n Kaifman	Scalin C	A. Lazrus

Investigator	University/Institution	Project Description
C. Leovy	University of Washington	Nimbus G. LIMS data analysis
J. London	University of Colorado	Analysis of ozone observations and theoretical considerations
M. Loewenstein	NASA/Ames Research Center	In situ ozone and nitric oxide measurements
M. Loewenstein	NASA/Ames Research Center	Chemiluminescent measurements of stratospheric species
J. Mangus	NASA/Goddard Space Flight Center	Optical dispersing elements for UV and BUV range
K. Mauersberger	University of Minnesota	Stratospheric measurements with a mass spectrometer between 1545 km
M. McCormick	NASA/Langley Research Center	SAGE experiment
M. McElroy	Harvard University	Measurements of $N_2O$ in lower troposphere and in various ocean and coastal waters
M. McElroy	Harvard University	Modeling of stratospheric constituents
A. Meinel	Helio Associates	UV spectrum
R. Menzies	Jet Propulsion Laboratory	Laser heterodyne radiometer detection of stratospheric species
J. Millard	NASA/Ames Research Center	Grab sampling of stratospheric methane
M. Molina	University of California, Irvine	Kinetics and photochemistry of stratospheric species
W. Moore	Utah State University	Negative ion mass spectrometry
M. Mumma	NASA/Goddard Space Flight Center	Stratospheric monitoring with an infrared heterodyne spectrometer
D. Murcray	University of Denver	Stratospheric balloon measurements of CFCI <sub>3</sub> and CF <sub>2</sub> CI <sub>2</sub>
A. Nagy	University of Michigan	Theoretical and experimental investigations of the ionosphere
W. Neupert	NASA/Goddard Space Flight Center	EUV instrumentation for rocket and shuttle application
R. Nicholls	York University	Detection of CIO using ground-based ultraviolet spectroscopy
J. Nisbet	Pennsylvania State University	Electron densities in the ionosphere

Investigator	University/Institution	Project Description
G. Northram	NASA/Langley Research Center	Lidar composition studies
R. Novick	Columbia University	Quiet sun x-ray background spectra
J. Park	College of William and Mary	HALOE theory and analysis
W. Parkinson	Harvard College Observatory	UV spectrum from sounding rockets
T. Pepin	University of Wyoming	SAGE, SAMII, and balloons
P. Perkins	NASA/Lewis Research Center	The Global Air Sampling Program (GASP)
E. Petrosiam	Stanford University	Energy release, mechanism, and terrestrial effects of solar flares
G. Pimentel	University of California, Berkaley	Infrared spectroscopy
W. Planet	NOAA/NESS	Nimbus G LIMS data analysis
G. Plass	University of Texas	Radiation transfer mathematics
A. Potter	NASA/Johnson Space Center	Spectroscopy of planetary atmospheres and comets
R. Prinn	Massachusetts Institute of Technology	Modeling of Space Shuttle effects on the stratosphere
V. Ramanathan	George Washington University	Radiative transfer
R. Rasmussen	Washington State University	Tropospheric measurements of nitrogen and chlorine compounds
R. Rasmussen	Washington State University	Halocarbon analysis and measurement techniques
E. Remsberg	NASA/Langley Research Center	Lidar composition studies
W. Rense	University of Colorado	UV spectrum
R. Reynolds	NASA/Ames Research Center	Optimization of dynamics in three dimensional models
C. Riegel	San Jose State University	Modeling support
J. Rosen	University of Wyoming	Aerosol measurements and analysis
S. Rowland	University of California, Irvine	Halogen analysis

Project Description	LACATE, Nimbus G, HALOE	SAGE data analysis	Reaction kinetics	Experimental and theoretical studies of stratospheric energetics	Modeling and assessment	Study of BUV ozone data from atmospheric Explorer-E	Model development and parameter studies	Assessment and model evaluations	Modeling support	Lidar measurements of atmospheric aerosols	Laboratory spectra of stratospheric species	ctrum	Model development	Data reduction algorithms	Vapor pressure of species at stratospheric temperatures	Theoretical study of transport processes in the ionosphere	Laser fluorescence technique applied to stratospheric species	Microwave Limb Sounder development	Microwave radiometer measurements of stratospheric species	Laboratory facility for the measurement of rate constants
Project	LACAT	SAGE d	Reaction	Experim	Modelin	Study o	Model d	Assessm	Modelin	Lidar m	Laborat	UV spectrum	Model o	Data re	Vapor p	Theore	Laser fl	Microw	Microw	Labora
University/Institution	NASA/Langley Research Center	Stanford Research Institute	York University	University of Michigan	NASA/Ames Research Center	NASA/Goddard Space Flight Center	NASA/Goddard Space Flight Center	NASA/Goddard Space Flight Center	Stanford University	NASA/Langley Research Center	Jet Propulsion Laboratory	Naval Research Laboratory	R and D Associates	Old Dominion University	Clark College	Cornell University	Ford Metor Company	Jet Propulsion Laboratory	Jet Propulsion Laboratory	Jet Propulsion Laboratory
Investigator	J. Russell	P. Russell	H. Schiff	W. Sharp	T. Shimazaki	N. Spencer	R. Stewart	R. Stolarski	J. Streiter	E. Sullivan	R. Toth	R. Tousey	R. Turco	J. Twitty	G. Walker	J. Walker	C. Wang	J. Waters	J. Waters	R. Watson

### Department of Defense Funded Research Projects

Project Description

University /Institution

Investigator

Balloon measurements of positive and negative ions by mass spectrometry	Atmospheric temperature measurements	Measurement of ${ m CO_2}$ between 30-60 km	Measurements of positive and negative ions using blue Gerdlen probes	Balloon and aircraft measurements of $ H_2  O$ using frost point hygrometry	Infrared spectroscopic measurement of stratospheric species from balloon	Ozone measurements with chemiluminescent ozonesonde from surface to 30 km	Ozone measurements by ground-based microwave radiometry	Solar flux measurements
University of Denver	Atmospheric Science Laboratory	Atmospheric Science Laboratory	Pennsy Ivania State University	Naval Research Laboratory	University of Denver	Atmospheric Science Laboratory	Naval Research Laboratory	Atmospheric Science Laboratory/ Panametrics
R. Amme	H. Ballard	H. Ballard	L. Hale	H. Mastenbrook	D. Murcray	J. Randhawa	J. Schwartz	B. Sellers

J. Swinnerton

Naval Research Laboratory

Gas chromatographic measurements of the chlorofluoromethanes

# Energy Research And Development Administration Funded Research Projects

Investigator	University /Institution	Project Description
A. Breslin	ERDA/Health and Safety Laboratory	Evaluation and calibration of stratospheric air sampling devices
C. Burnett	Florida Atlantic University	Daytime spectroscopic measurements of the upper atmosphere
A. Castleman Jr.	University of Colorado	Heterogeneous Nucleation: The Properties of Small Clusters and Atmospheric lons
J. Chang	Lawrence Livermore Laboratory	Model assessment of the potential consequences of high yield atmospheric nuclear explosions
R. Cicerone	University of Michigan	The role of chlorofluorocarbons and nitrous oxide in atmospheric chemistry—Whole air sampling
J. Clark	Pennsylvania State University	Stratospheric and mesospheric disturbances of circumpolar flows
R. Craig	Florida State University	Analysis of vertical ozone measurements
R. Duce	University of Rhode Island	Atmospheric chemistry of the halogens: natural and anthropogenic
S. Falkowski	Air Force Geophysics Laboratory	Project Ash Can—Balloon-borne sampling of radioactive and stable trace constituents
E. Good	Air Force Geophysical Laboratory	Balloon and rocket-borne messurements of small scale turbulence
P. Guthals	Los Alamos Scientífic Laboratory	Field support of Project Airstream sampling systems
J. Friend	Drexel University	Laboratory studies of the formation of aerosols and their interaction with gases
W. Gordon	Rice University	Observation and interpretation of winds in the stratosphere and mesosphere
J. Gray	Argonne National Laboratory	Research on molecular sieves for applicability to sample trace gas constituents
A. Green	University of Florida	Atmospheric radiative transfer and atomic processes
J. Heicklen	Pennsylvania State University	Chemical reactions of importance in the Earth's atmosphere
G. Hidy	Environmental Research and Technology Inc.	An atmospheric air quality model of sulfate formation.
C. Hochanadel	Oak Ridge National Laboratory	Flash photolysis study of elementary reactions in gas phase systems
H. Johnston	Lawrence Livermore Laboratory	Assessment of the vulnerability of stratospheric $O_{\mathfrak{s}}$ to human activities

# Energy Research and Development Administration Funded Research Projects (Continued)

Investigator	University /Institution	Project Description
H. Judeikis	Aerospace Corporation	Effects of heterogeneous reactions on the chemistry of the stratosphere (NO $_2$ , HCI, aerosols)
P. Krey	ERDA/Health and Safety Laboratory	Analysis and interpretation of Project Airstream and Project Ash Can data
D. Lamb	Desert Research Institute	The formation and modification of cloud nuclei by gas phase reactions
G. Lawrence	University of Colorado	Disassociation fragment spectroscopy by ultraviolet and electrons
A. Lilley	Harvard University	Measurement of stratospheric trace contaminants using millimeter wave spectroscopy
L. Machta	NOAA/Air Resources Laboratory	Interpretation and model development of Project Airstream and Project Ash Can data
C. Mathews	NASA/Johnson Space Center	Project Airstream—Aircraft-borne sampling of radioactive and stable trace constituents
M. McElroy	Harvard University	Aeronomical studies of planetary atmospheres
D. Murcray	University of Denver	The distribution with altitude in the stratosphere of fluorocarbons and odd nitrogen compounds
R. Newell	Massachusetts Institute of Technology	Establishment of background of climatic change and the influence on climate of anthropogenic effects
G. Ostlund	University of Miami	Study of the fate of tritium releases into the environment on global or local scales
J. Park	College of William & Mary	Distributions of minor gases in the stratosphere and the troposphere. A two-dimension atmospheric model
H. Poland	Colorado University	Atmospheric reactions of NO <sub>2</sub>
R. Prinn	Massachusetts Institute of Technology	Chemistry and chemical evolution of planetary atmospheres
K. Rahn	University of Rhode Island	Atmospheric chemistry of the halogens: natural and anthropogenic
E. Reiter	Institute for Atmospheric Environmental Research	Study of stratospheric, troposher exchange using cosmogenic nuclides as tracers
F. Rowland	University of California—Irvine	Effects upon stratospheric ozone of antropogenic chlorine atoms released from chlorofluomethanes
W. Sedlacek	Los Alarnos Scientific Laboratory	Airborne tunable dye-laser lidar system to measure altitude profiles of trace constituents
R. Stedman	University of Michigan	Tropospheric Chemistry—Field measurements and optimal model
C. Stevens	Argonne National Laboratory	cryogenics gas flow system for balloon-borne collection of trace gases

# Energy Research and Development Administration Funded Research Projects (Continued)

Project Description

University/Institution

Investigator

Linear and nonlinear spectroscopic studies of OH, H, O, and HO,	Linear and nonlinear spectroscopic studies of OH, H <sub>2</sub> O, and HO <sub>2</sub>	Accelerated crossed molecular beam study of elementary processes in the upper atmosphere	Statistical theory of scattering by dielectric particles	Development of flyable gas chromatograph for balloon-borne measurement of fluorocarbons
University of Michigan/Ford	University of Michigan	Argonne National Laboratory	Charles Stark Draper Laboratory	Sandia Laboratories
C. Wang	J. Ward	S. Wexier	C. Whitney	R. Woods

## Environmental Protection Agency Funded Research Projects

	Investigator	University /Institution	Project Description
	L. Hale	Air Force Geophysical Laboratory	Balloon-borne spectrometer measurements of the solar flux
	P. Hanst	EPA/Environmental Sciences Research Laboratory	Measurement of trace gases at urban, rural and maritime locations
	K. Mani	Northrup Corporation	Infrared correlation spectroscopy
	R. Narcisi	Air Force Geophysical Laboratory	Balloon-borne cryogenic gas sampler for stratospheric species
	J. Pitts, Jr.	University of California, Riverside	In situ infrared absorption spectroscopy
	R. Rasmussen	Washington State University	Measurement of halogenated compounds in rural and urban areas, and over water
	J. Shaw	Ohio State University	Rates of photo-oxidation of halogenated compounds
48	H. Singh	Stanford Research Institute	Tropospheric distribution of halocarbons
	I. Soloman	Illinois Institute of Technology	Laboratory experiments to determine rates of degradation of halocarbon pollutants

### Federal Aviation Administration Funded Research Projects

Project Description

Institution/University

Investigator

P. Athens	A. D. Little Co.	Global aircraft emissions loading data for FAA fleet projections
J. Davenport	Stanford Research Institue	Laboratory studies of $NO_2$ photolysis, absorption cross sections and quantum yields
A. Fontijn	AeroChem Research Laboratories, Inc.	Reaction rates of NO $_2$ + O( $^4$ D) and HNO $_2$ + O $_3$
D. Garvin and R. Hampson	National Bureau of Standards	Photochemical data evaluation
J. Gille and L. Heidt	National Center for Atmospheric Research	Trace gas measurements by cryogenic sampling
R. Greenstone	Operations Research, Inc.	Technical information and documentation
P. Guthals and D. Murcray	Los Alamos Scientific Laboratory/University of Denver	Processing of April and May 1975 Airstream data
A. Harker	Rockwell International Corp.	Laboratory studies of $O_3$ decomposition and $HNO_3$ formation in the presence of $H_2SO_4$ mist
D. Hofmann and J. Rosen	University of Wyoming	USA/USSR cooperative stratospheric serosol research
D. Hofmann	University of Wyoming	NO balloon messurement support
E. Kaiser	Ford Motor Company	Rate coefficients for $HNO_2 + O_3$ and $O(^3P) + N_2O_5$
F. Luther and J. Lovill	Lawrence Livermore Laboratory	Modeling and analysis of Block 5D ozone data
R. Oliver	Institute for Defense Analyses	Assessment of stratospheric effects and uncertainties
R. Penndorf	Private Consultant	Analysis of measurement requirements
H. Schiff	York University	Rate coefficients for $N_2$ $0+O(^1D)$ and $O(^3P)+N_2O_{\mathfrak{g}}$
R. Pozdena	Stanford Research Institute	International air traffic forecast
A. Broderick	Transportation Systems Center	High Altitude Pollution Program support
G. Widhopf	Aerospace Corporation	2D modeling

# National Oceanic and Atmospheric Administration Funded Research Projects

Project Description

Institution

Aeronomy Laboratory	Whole air sampling (gas chromatography/electron capture detector) of atmospheric species including CFMs
	Balloon-borne resonance fluorescence of CIO
	Ground-based measurements of $NO_2$ by atmospheric absorption
	Ground-based measurements of NO by chemiluminescence
Air Resources Laboratory	Ozonesonde vertical profiles
Global Monitoring for Climatic Change Stations	Ground-based measurements of F-11, CCl $_4$ , O $_3$ solar flux, particulates

### National Science Foundation Funded Research Projects

Investigator	University/Institution	Project Description
C. Burnett	Florida Atlantic University	Daytime spectroscopic measurements of the upper atmosphere
A. Castleman, Jr.	University of Colorado	Heterogeneous nucleation: The properties of small clusters and atmospheric ions
R. Cicerone	University of Michigan	Role of CFMs and N <sub>3</sub> O in atmospheric chemistry
J. Clark	Pennsylvania State University	Stratospheric and mesospheric (dynamic) disturbances
R. Craig	Florida State University	Analysis of ozone measurements
J. Friend	Drexel University	Chemical reactions in the stratosphere and troposphere
W. Gordon	Rice University	Observation and interpretation of winds in the stratosphere and mesosphere
A. Green	University of Florida	Radiative transfer in a cloudy atmosphere and electron collision cross sections
J. Heicklen and R. Simonaitis	Pennsylvania State University	Laboratory studies of O <sup>1</sup> (D), OH, HO <sub>2</sub> reactions and O <sub>3</sub> photolysis
G. Hidy	Environmental Science and Technology, Inc.	Atmospheric model of sulfate formation
H. Judeikîs	Aerospace Corporation	Heterogeneous reactions and stratospheric chemistry
D. Lamb	Desert Research Institute	Formation and modification of cloud nuclei by gas phase reactions
G. Lawrence	University of Colorado	Laboratory studies of photon and electron dissociation of trace gases
A. Lilley	Harvard University	Measurement of stratospheric trace species by millimeter wave spectroscopy
M. McElroy	Harvard University	Aeronomical studies of planetary atmospheres
D. Murcray	University of Denver	Vertical profiles of minor constituents
J. Park	College of William and Mary	2-D atmospheric model
R. Prinn	Massachusetts Institute of Technology	Chemical evolution of phanetary atmospheres
K. Rahn and R. Duce	University of Rhode Island	Atmospheric halogen chemistry

# National Science Foundation Funded Research Projects (Continued)

Tropospheric Chemistry	Spectroscopic studies of OH, H <sub>2</sub> 0, HO <sub>2</sub>	Statistical theory of scattering
University of Michigan	University of Michigan	The Charles Stark Draper Laboratory, Inc.
B. Stedman	J. Ward and C. Wang	C. Whitney

### Industry Funded Research & Project Descriptions (MCA)

	Investigator	University /Institution	Project Description
	Dr. John W. Birks	University of Illinois	Measurement of reaction rate constants at various temperatures to determine activation energies. Method used is a discharge flow technique with molecular beam mass spectrometry for detection purposes. Several reactions are to be measured involving chlorine atoms, CIO radicals, and hydrogen chloride.
	Dr. Malcolm J. Campbell and Dr. R. A. Rasmussen	Washington State University	Destruction rates of fluorocarbons by natural ionization processes (ion-molecule reactions). Fluorocarbon and chlorocarbon measurements in the northwestern U.S., over the Pacific Ocean, and Antarctica—including measurements in the ice cap. Analysis of halocarbons in "antique" air (samples trapped for many years).
	Dr. David T. Chang	Environmental Research & Technology	Modeling and sensitivity analyses related to the fluorocarbon/ozone question.
	Dr. Dereck M. Cunnold	Massachusetts Institute of Technology	A critique of models used to estimate chlorofluorocarbon effects on ozone.
	Dr. Douglas D. Davis	University of Maryland	Completed: An evaluation of laser induced fluorescence as a potential method for measurement of CIO radical concentrations in the stratosphere. The evaluation showed that this does not represent a practical method of measurement.  Continuing: Measurement of absorption cross-section of the CIO radical.
53	Dr. Phillip A. Ekstrom	Battelle Memorial Institute— Pacific Northwest Laboratories	Evaluation and demonstration of ground-based millimeter wavelength (93 GHz) observations of stratospheric chlorine oxide radical.
3	Dr. Carlton J. Howard	National Ocean and Atmospheric Administration (NOAA)	Laser magnetic resonance for CIO radical. Development and demonstration of laser magnetic resonance for CIO radical in the far infra-red region. CIO chemistry.
	Dr. James E. Lovelock	University of Reading (U.K.)	Completed: A study of the atmospheric concentrations of halocarbons over Western Europe and over the Atlantic Ocean. Continuing: Monitoring activities extending to halocarbons such as methyl halides.
	Dr. Volker Mohnen	State University of New York (Albany)	Investigation of ion-molecule reactions involving chlorine compounds in the troposphere and stratopshere.
	Dr. David G. Murcray	University of Denver	High resolution infra-red measurement of the stratospheric distribution of fluorocarbons, chlorocarbons, halogen compounds, and reactive intermediates. Measurements made in September on the STRATCOM flight are being analyzed (preliminary results were reported at American Geophysical Union meeting, December 12). Two additional flights made December 1975. Further flights planned.
	Dr. Ralph W. Nicholls	York University (Canada)	Laboratory studies of the infra-red vibration-rotation spectrum of the CIO radical. Ground-based high resolution atmospheric observation of the electronic spectrum of the CIO radical.
	Dr. James N. Pitts and Dr. O. C. Taylor	University of California (Riverside)	Completed: Measurements of atmospheric concentrations of fluorocarbons over southern California and in the lower stratosphere; reaction rates of fluorocarbons with O ( <sup>1</sup> D) atoms and OH radicals; and stability of fluorocarbons under photochemical smog conditions.  Continuing: Currently adapting an experimental chamber capable of simulating stratospheric conditions which will be used to observe the reaction between chlorine and ozone. Of particular emphasis is actual measurement of the catalytic chain length of the reaction, a key quantity in the models in terms of interpreting the significance of reactions between chlorine and ozone.

# Industry Funded Research & Project Descriptions (MCA) (Continued)

	Investigator	University /Institution	Project Description
	Dr. R. A. Rasmussen	Washington State University	See Dr. M. J. Campbell above.
	Dr. C. Sandorfy	University of Montreal (Canada)	<i>Completed:</i> Photoelectron and ultraviolet absorption spectra of fluorocarbons with relationship to high altitude photodissociation.
	Dr. Donald H. Stedman	University of Michigan	Completed: Laboratory studies have demonstrated the feasibility for detecting stratospheric chlorine oxide radicals by chemical conversion to chlorine atoms (by reactions with nitric oxide) accompanied by vacuum ultraviolet resonance fluoroscence.  Future: In-flight use of this technique may be supported by NASA.
	Dr. O. Clifton Taylor	University of California (Riverside)	See Dr. J. N. Pitts above.
	Dr. Brian A. Thrush	Cambridge University (U.K.)	User of laser magnetic resonance to study reactions of the $\mathrm{HO}_2$ radical at concentrations in the stratosphere of importance to the chlorine/ozone reaction. For example, a chain termination process is: $\mathrm{CI+HO}_2 \to \mathrm{HCI+O}_2$
54	Dr. Robert A. Young	Xonics, Inc.	Measurement of total stratospheric chlorine by resonance fluoroscence. The preliminary experiment was flown on the September STRATCOM balloon. Measurements of important chlorine species are to be made using resonance scattering and photo fragmentation apparatus. NASA is funding Xonics, Inc., to construct a stratospheric simulator and to develop a titration instrument (c. f. Stedman) for chlorine oxide capable of being flown on a U-2 aircraft.